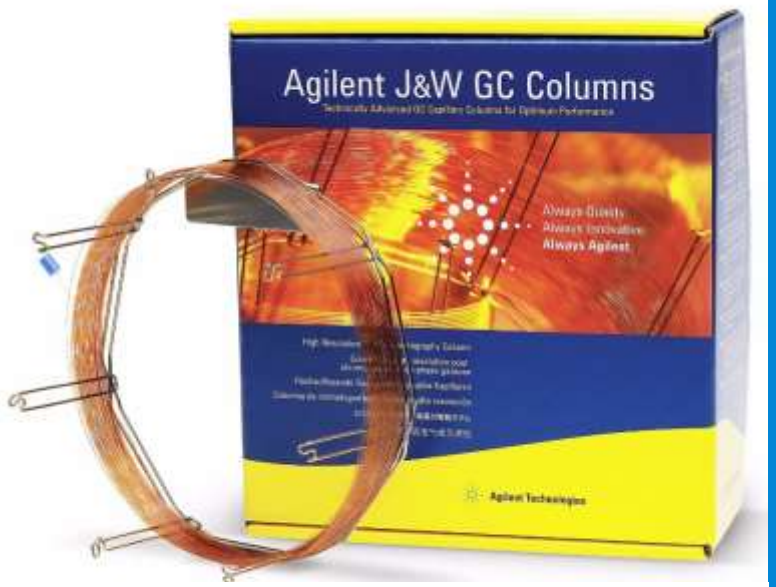
Chromatography in the Fast Lane

Fast GC

Mark Sinnott
Application Engineer
December 13, 2018



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Trusted Answers

Questions to Ask

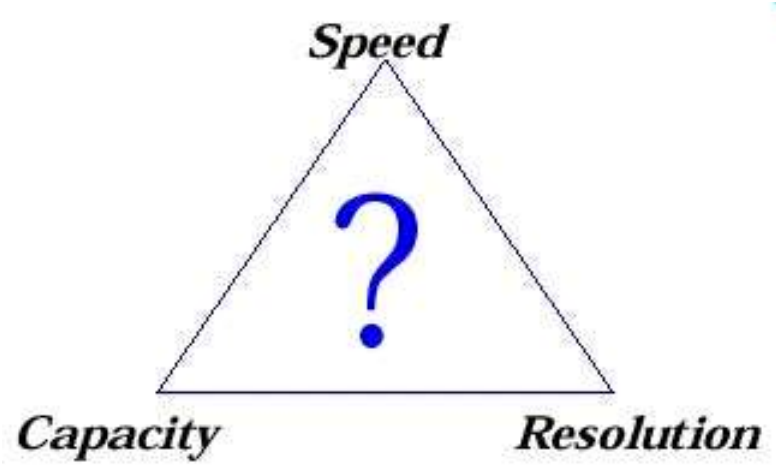
What information do you need from your analysis?

Do you have more baseline than you need between your peaks?

Do you need to resolve all of the components?

Variables for Shortening Run Times

- Stationary Phase
- Temperature Programming
- Carrier Gas: type and linear velocity
- Shorten Column Length
- Decrease Film Thickness
- Decrease Internal Diameter



Resolution

$$R_S = \frac{\sqrt{N}}{4}\left(\frac{k}{k+1}\right)\left(\frac{\alpha-1}{\alpha}\right)$$

Factors effecting R_s	
Efficiency	**N = f (gas, L, r_c)**
Retention	**k = f (T, d_f, r_c)**
Selectivity	**α = f (T, phase)**

Variables	
L	**Length**
r_c	**radius**
d_f	**film thickness**
T	**Temperature**

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Stationary Phase - Common Types

Siloxane polymers

Poly(ethylene) glycols

Porous polymers

Selectivity

Relative spacing of the chromatographic peaks

The result of all non-polar, polarizable and polar interactions that cause a stationary phase to be more or less retentive to one analyte than another

Optimizing Selectivity

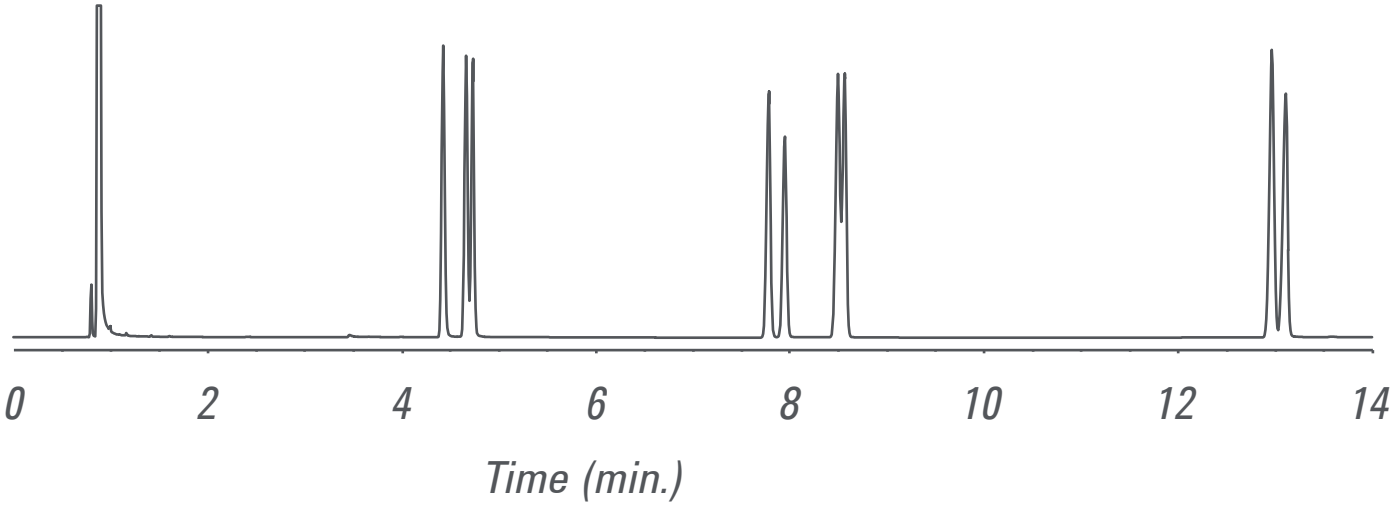
Match analyte polarity to stationary phase polarity

- **like dissolves like(oil and water don’t mix)**

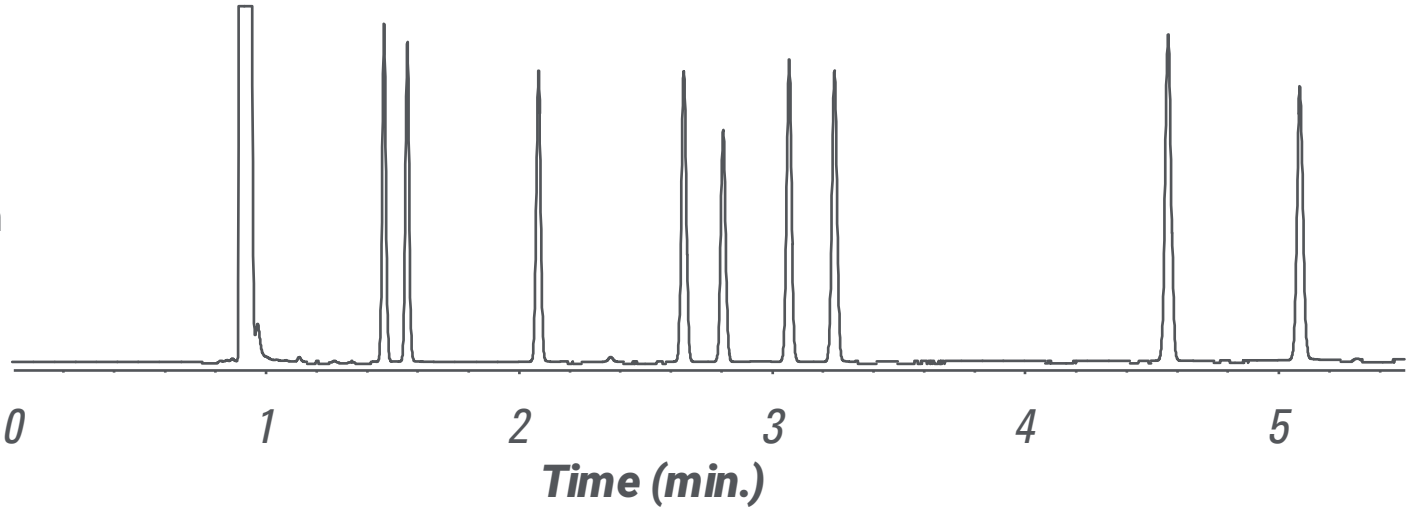
Take advantage of unique interactions between analyte and stationary phase functional groups

Start with the Right Phase

DB-1
15m x 0.32mm, 0.25µm
Oven:
40°C for 2 min
40-120°C at 5°C/min



DB-Wax
15m, 0.32mm, 0.25µm
Oven:
80-190°C at 20°C/min



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Variables	
L	Length
r_c	radius
d_f	film thickness
T	Temperature

Column Length and Efficiency (Theoretical Plates)

Length (m)	n
15	69,450
30	138,900
60	277,800

0.25 mm ID
n/m = 4630 (for k = 5)

Column Length and Resolution

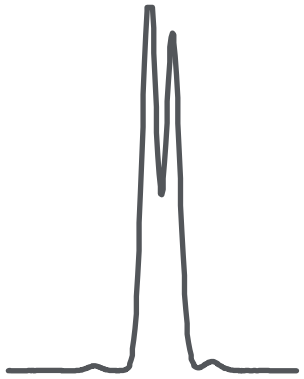
$$R \alpha \sqrt{n} \alpha \sqrt{L}$$

Length X 4 = Resolution X 2

$$t \alpha L$$

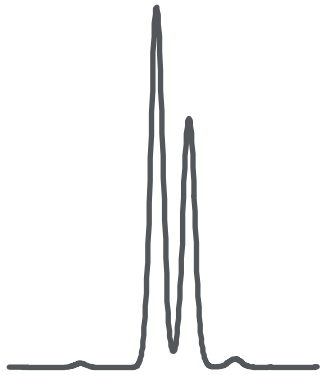
Column Length VS Resolution and Retention: Isothermal

R=0.84
2.29 min



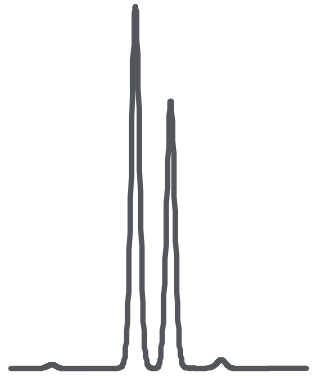
15 m

R=1.16
4.82 min



30 m

R=1.68
8.73 min

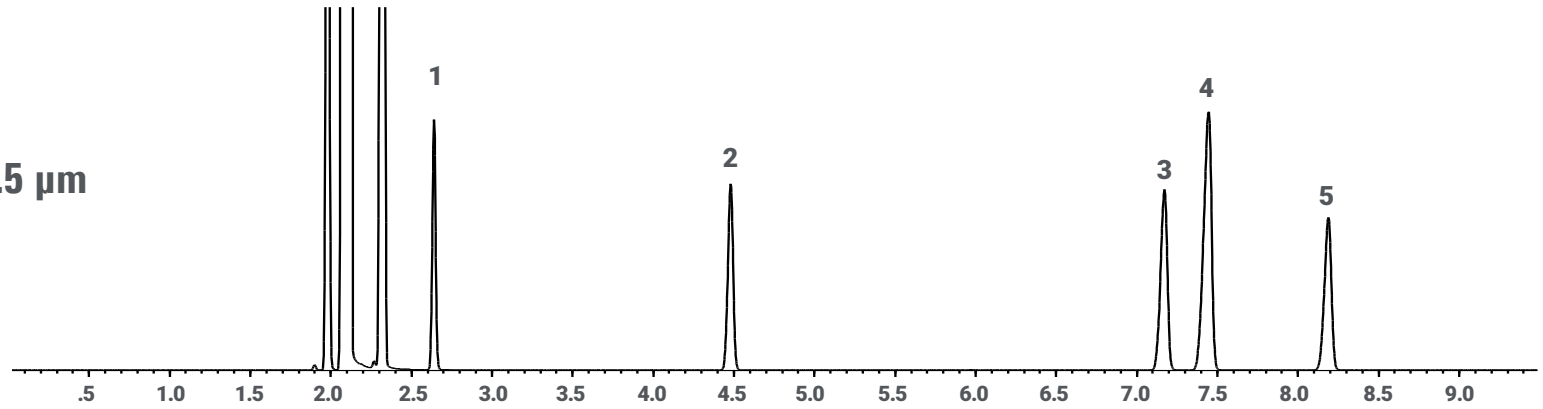


60 m

Double the plates, double the time but not double the the resolution

DECREASE THE LENGTH

DB-5
30 m
0.53 mm I.D., 0.5 µm



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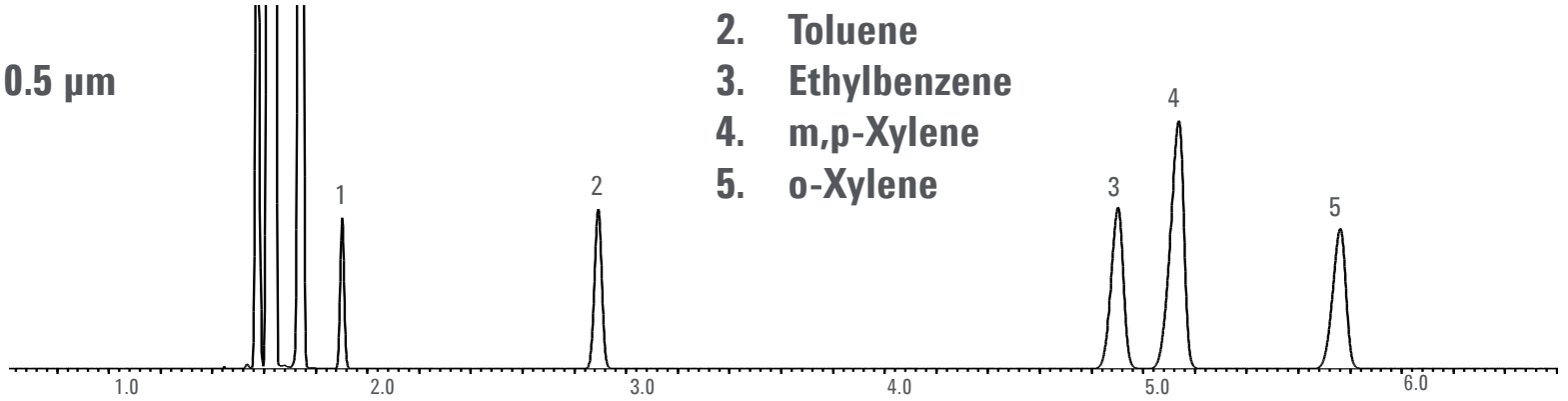
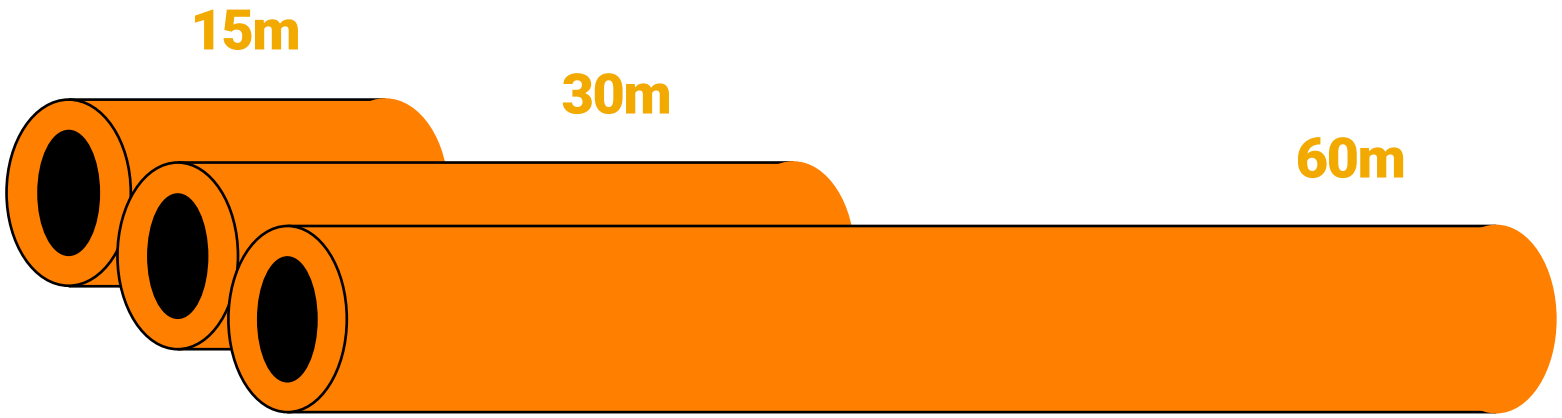


1. Benzene
2. Toluene
3. Ethylbenzene
4. m,p-Xylene
5. o-Xylene

BTEX
Carrier: Helium, 36 cm/sec at 40°c
Oven : 40°C for 3 min, 5°/min to 100°C

Column Length and Cost



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Length Summary

If you Decrease Length:	
Efficiency	Decrease
Resolution	Decrease
Analysis Time	Decrease
Pressure	Decrease
Cost	Decrease

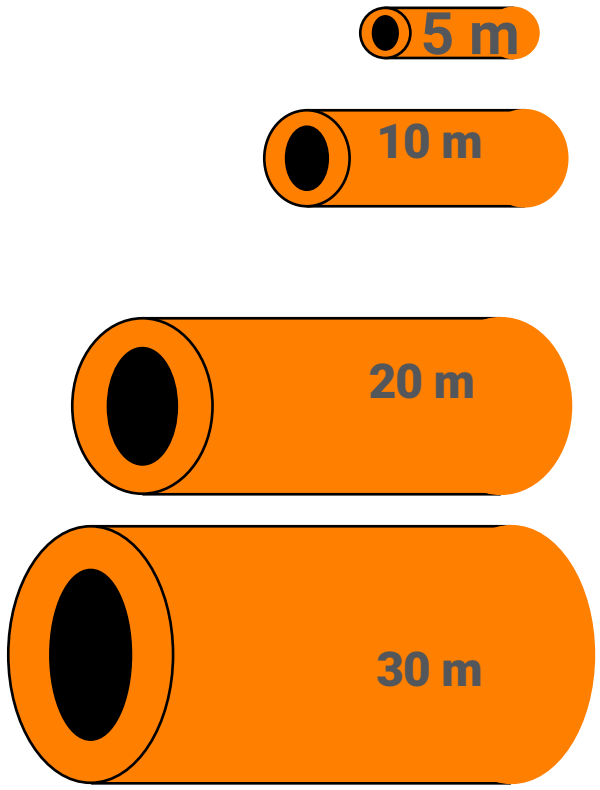
Resolution

$$R_S = \frac{\sqrt{N}}{4}\left(\frac{k}{k+1}\right)\left(\frac{\alpha-1}{\alpha}\right)$$

Factors effecting R_s	
Efficiency	**N = f (gas, L, r_c)**
Retention	**k = f (T, d_f, r_c)**
Selectivity	**α = f (T, phase)**

Variables	
L	Length
r_c	radius
d_f	film thickness
T	Temperature

Column Diameter - Theoretical Efficiency

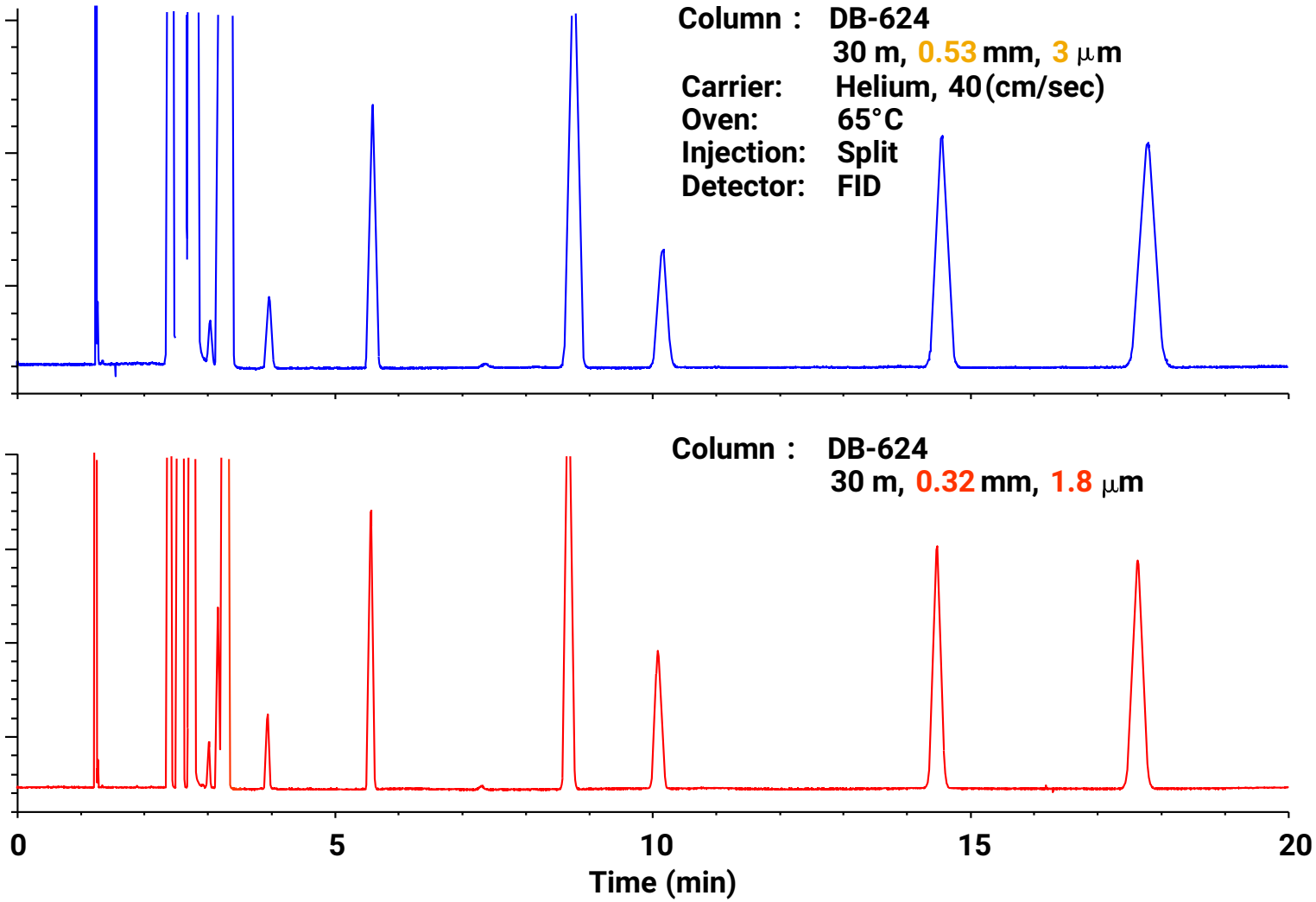


Total Plates	I.D. (mm)	n/m
N ~ 112,000	0.05	23,160
N ~ 112,000	0.10	11,580
	0.18	6,660
N ~ 112,000	0.20	5830
	0.25	4630
N ~ 112,000	0.32	3660
	0.45	2840
	0.53	2060

k = 5

Different Column I. D.

Equal Phase Ratios



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PHASE RATIO (β)

Film Thickness

Column Dimensions	Phase Ratio β
30 m x .53 mm x 3.0 μm	44
30 m x .32 mm x 1.8 μm	44

$$K_C = k\beta$$

$$\beta = \frac{r}{2d_f}$$

Column Diameter and Capacity

I.D. (mm)	Capacity (ng)
0.05	1-2
0.10	6-13
0.18	25-55
0.20	35-70
0.25	80-160
0.32	110-220
0.45	600-800
0.53	1000-2000

Like Polarity
Phase/Solute
0.25 µm film thickness

Column Diameter - Inlet Head Pressures (Helium)

I.D (mm)	Pressure (psig)
0.05	275-400
0.10	90-130
0.18	30-45
0.20	25-40
0.25	15-25
0.32	10-20
0.45	3-7
0.53	2-4

30 meters
Hydrogen pressures x 1/2

Column Diameter and Carrier Gas Flow

Lower flow rates: Smaller diameter columns

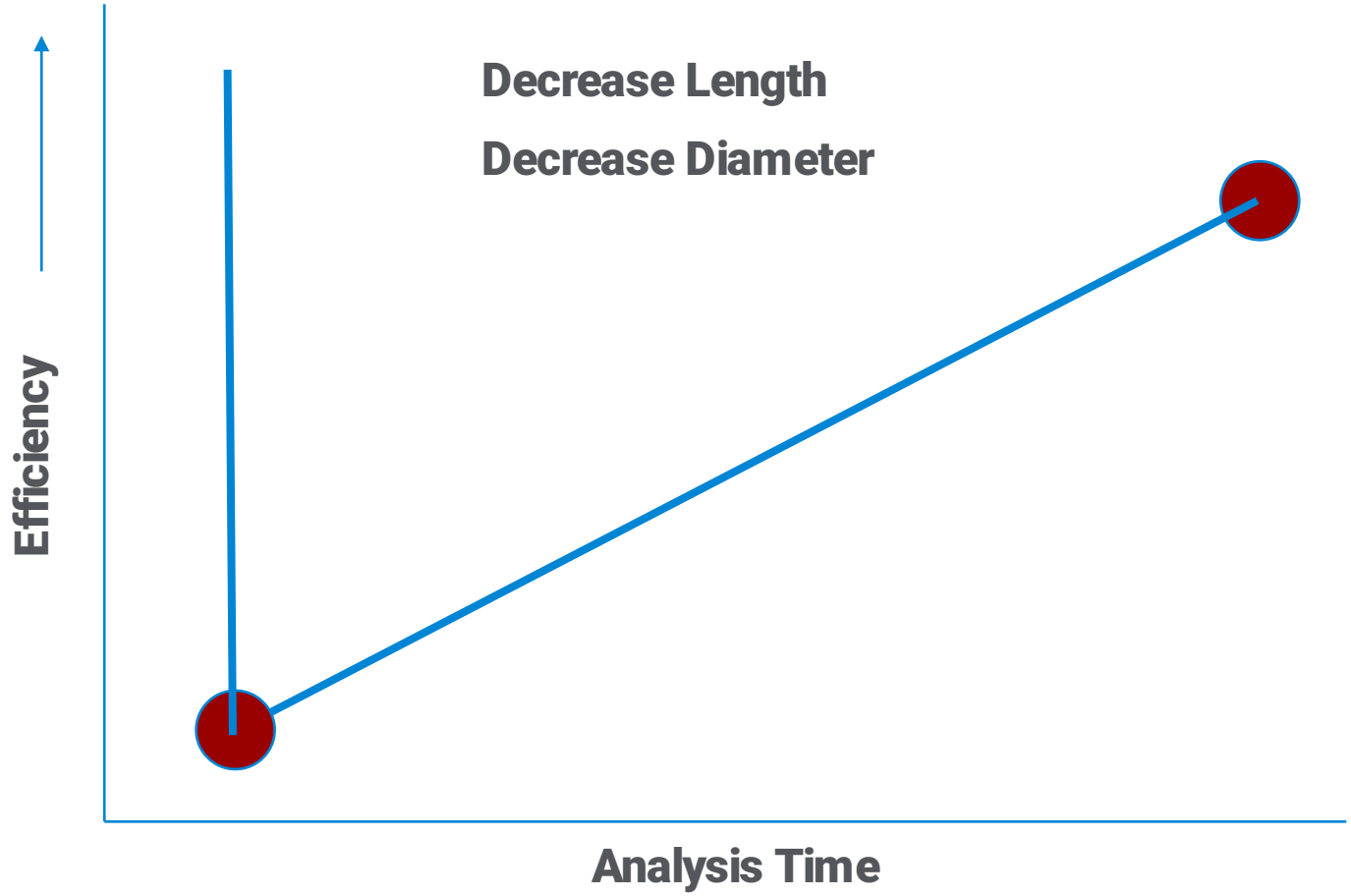
Higher flow rates: Larger diameter columns

Low flow rates : GC/MS
High flow rates: Headspace, purge & trap

Diameter Summary

If you decrease the inside diameter:	
Efficiency	Increase
Resolution	Increase
Pressure	Increase
Capacity	Decrease
Flow rate	Decrease

Combining a change in Length with a change in Diameter



Carrier Gas Considerations
Best velocity?

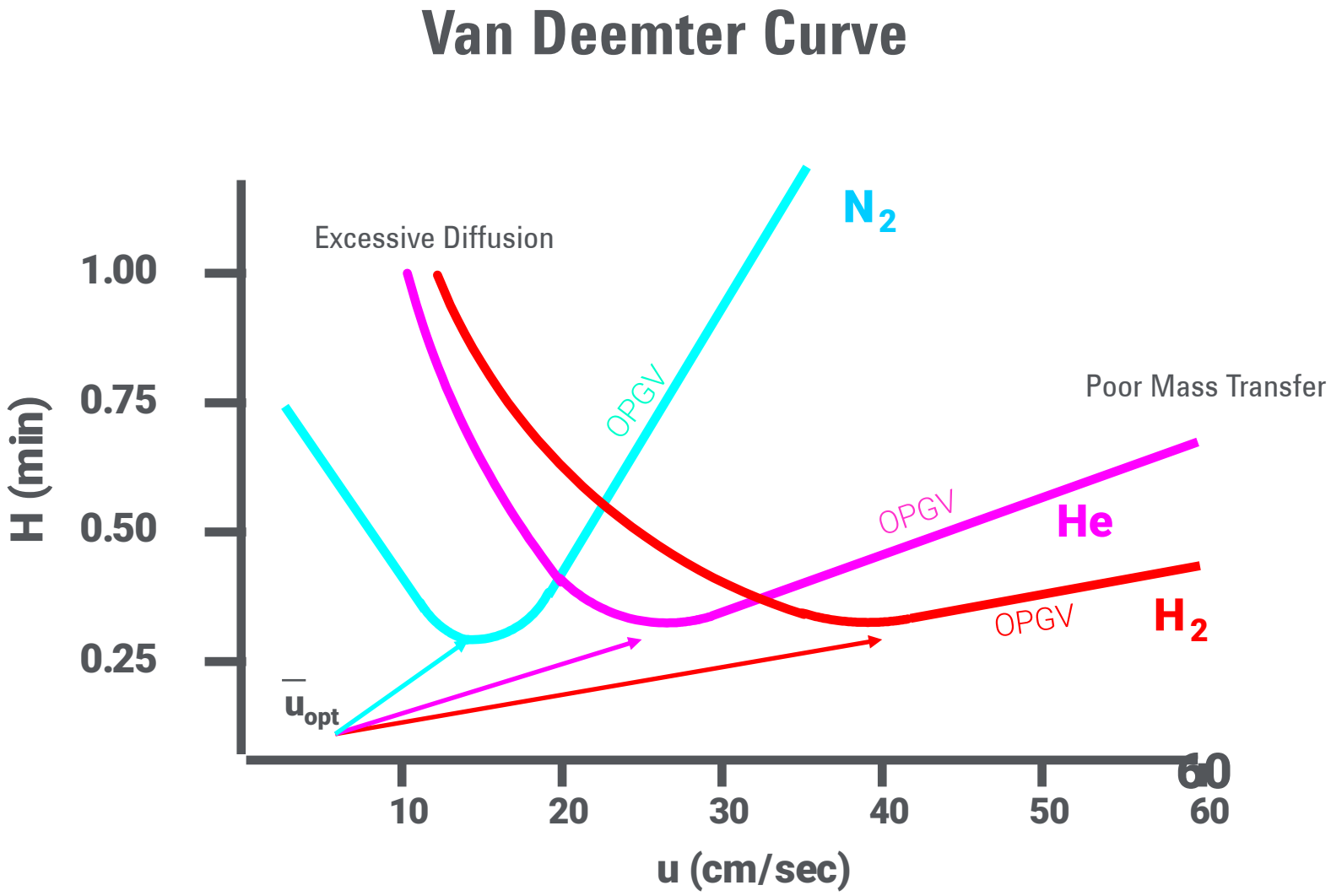
Optimal range of velocities

Too low or high results in loss of resolution

Balance resolution and analysis time

BUT… there is no LAW against going FASTER

Carrier Gas Considerations



Carrier Gas Considerations

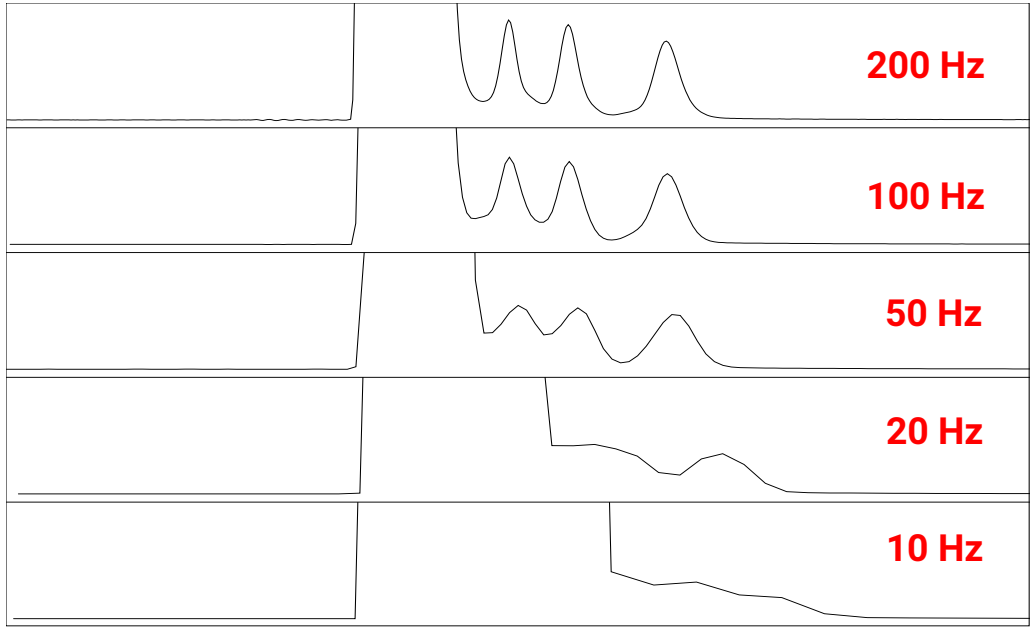
Utilizing Computer Controlled Flow Ramping (EPC)

Lonely Late Eluters? = P 

Decrease retention and overall run time by increasing pressure

(speed up the gas!)

Fast Detector Electronics – 6890 FID



Proper peak quantitation typically requires a minimum of 10 data points per peak

10 Hz data rate: (peaks less than one second wide will have less than 10 data points)

200 Hz data rate: (peaks as narrow as 50 msec can be handled reliably)

Easy Options with Method Translation Software

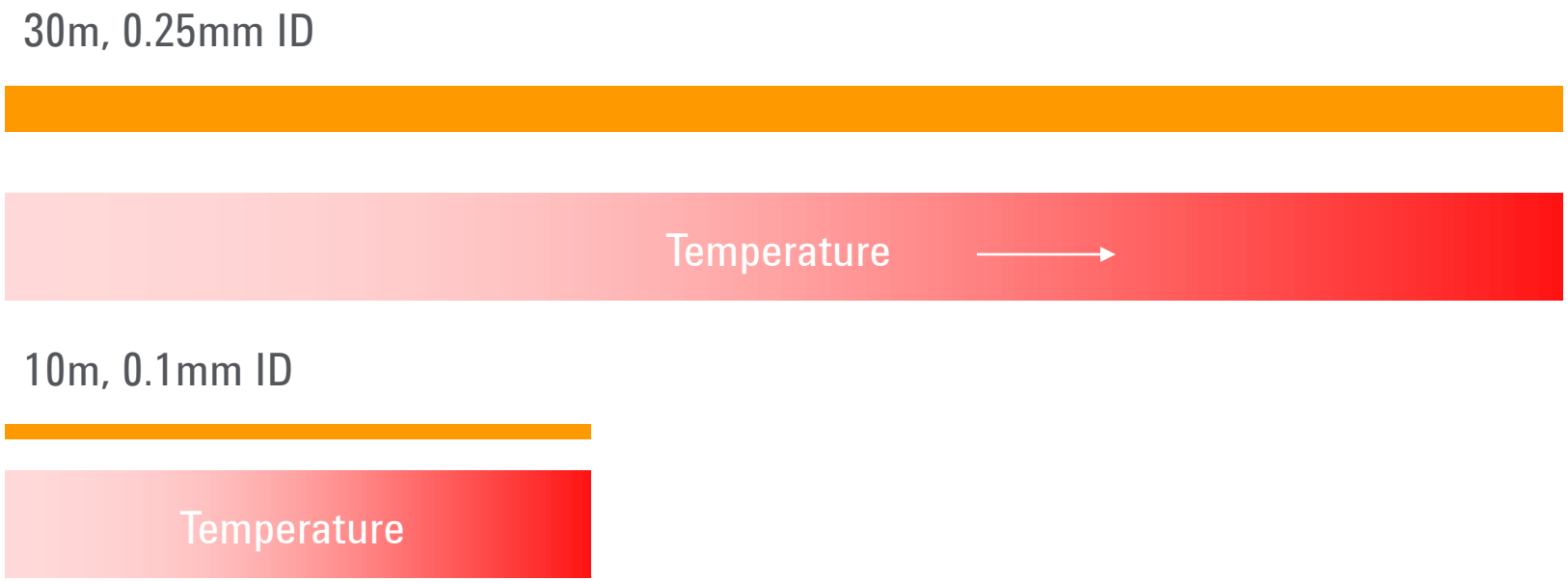
Different Column Dimensions

Switch He to H_2 Carrier Gas and Try Faster Velocities

Same Column & Gas Type but Faster Velocities

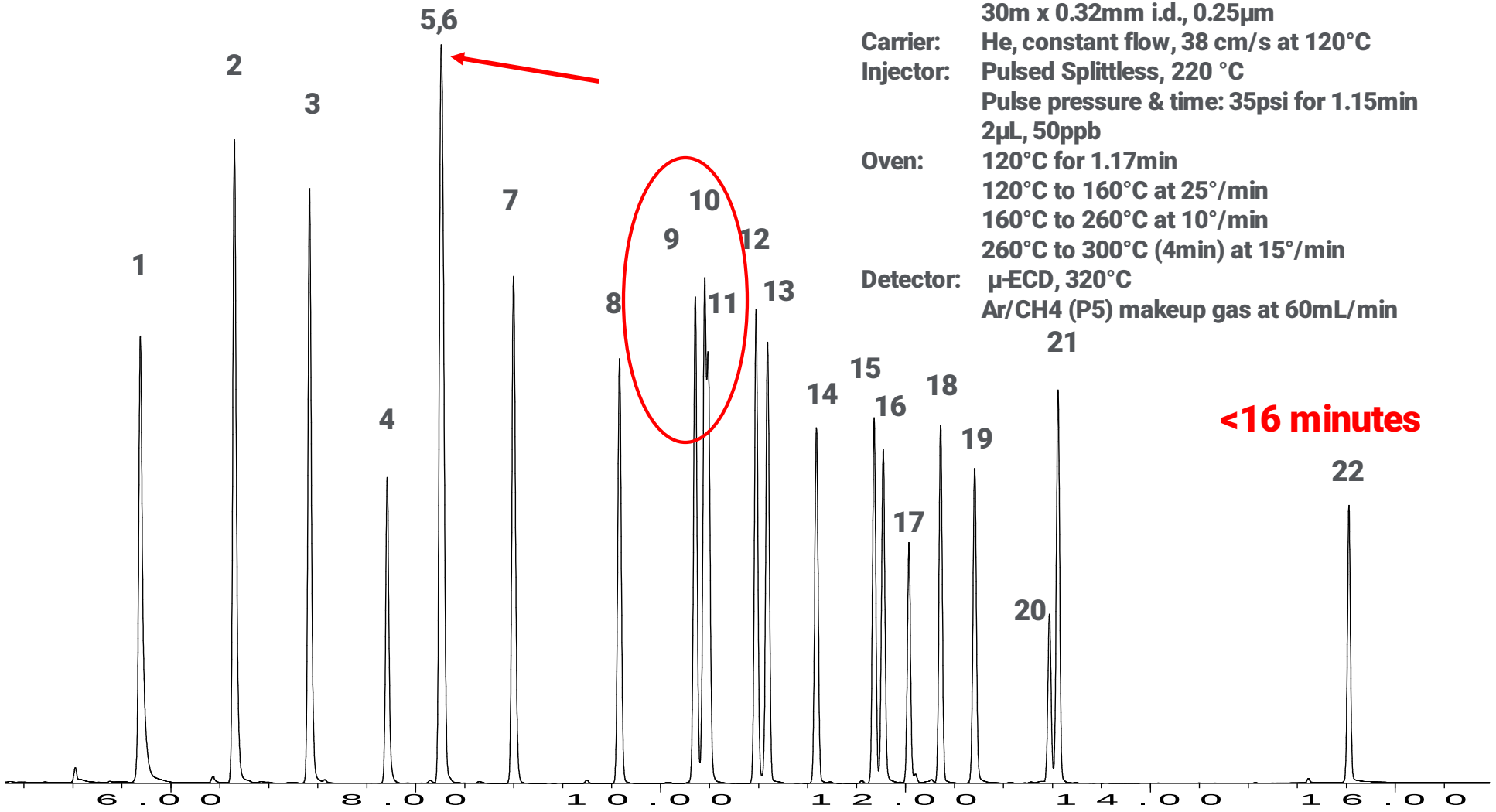
Combination of all of the above

Temperature Programming



Temperature program must be modified to give same temperature of elution (i.e. faster ramps, shorter hold times)

CLP-Pesticides - Original “Improved” Method 0.32mm I.D., Helium Carrier Gas



Column: DB-XLB
30m x 0.32mm i.d., 0.25µm
Carrier: He, constant flow, 38 cm/s at 120°C
Injector: Pulsed Splittless, 220 °C
Pulse pressure & time: 35psi for 1.15min
2µL, 50ppb
Oven: 120°C for 1.17min
120°C to 160°C at 25°/min
160°C to 260°C at 10°/min
260°C to 300°C (4min) at 15°/min
Detector: µ-ECD, 320°C
Ar/CH4 (P5) makeup gas at 60mL/min

<16 minutes

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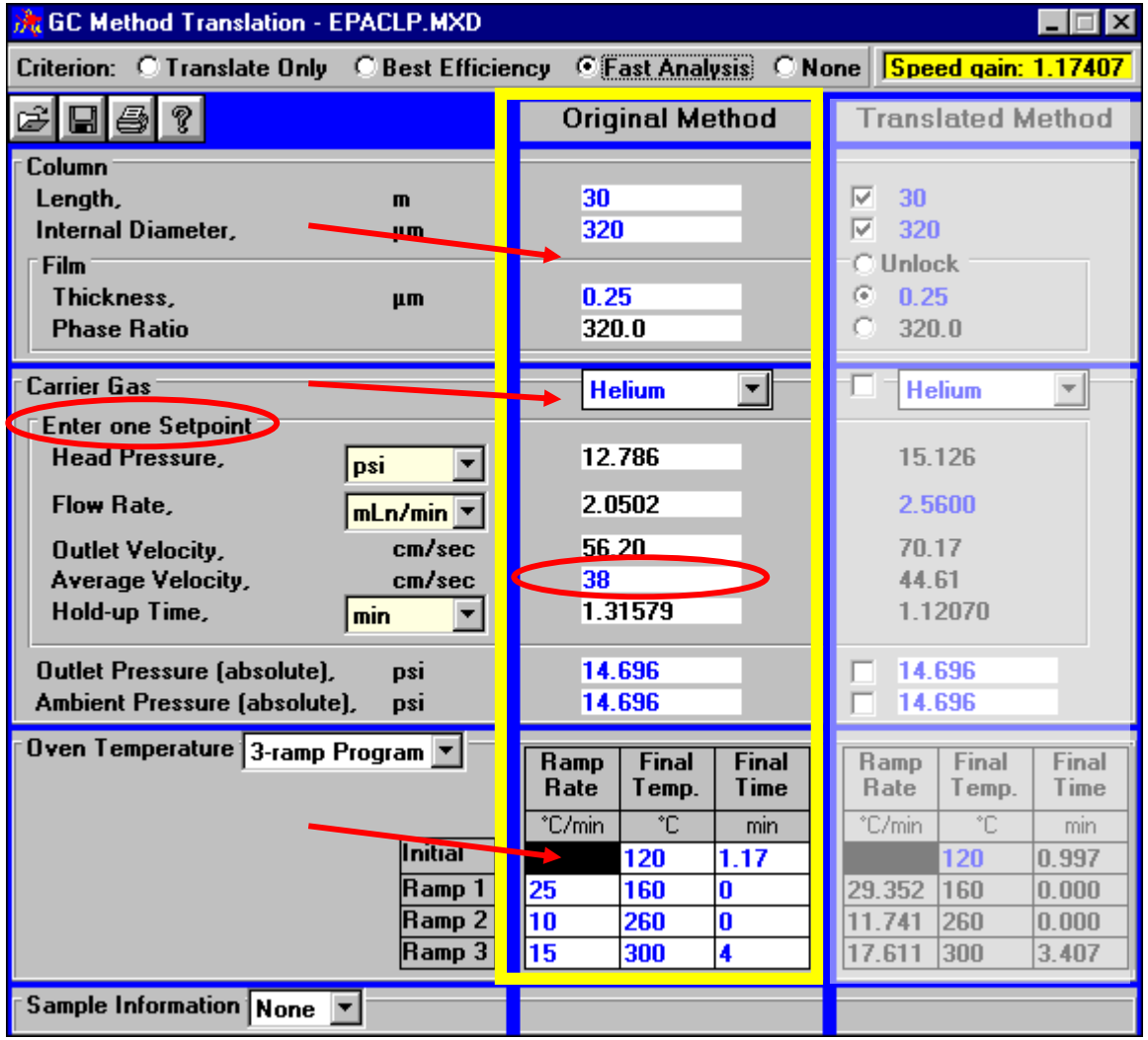
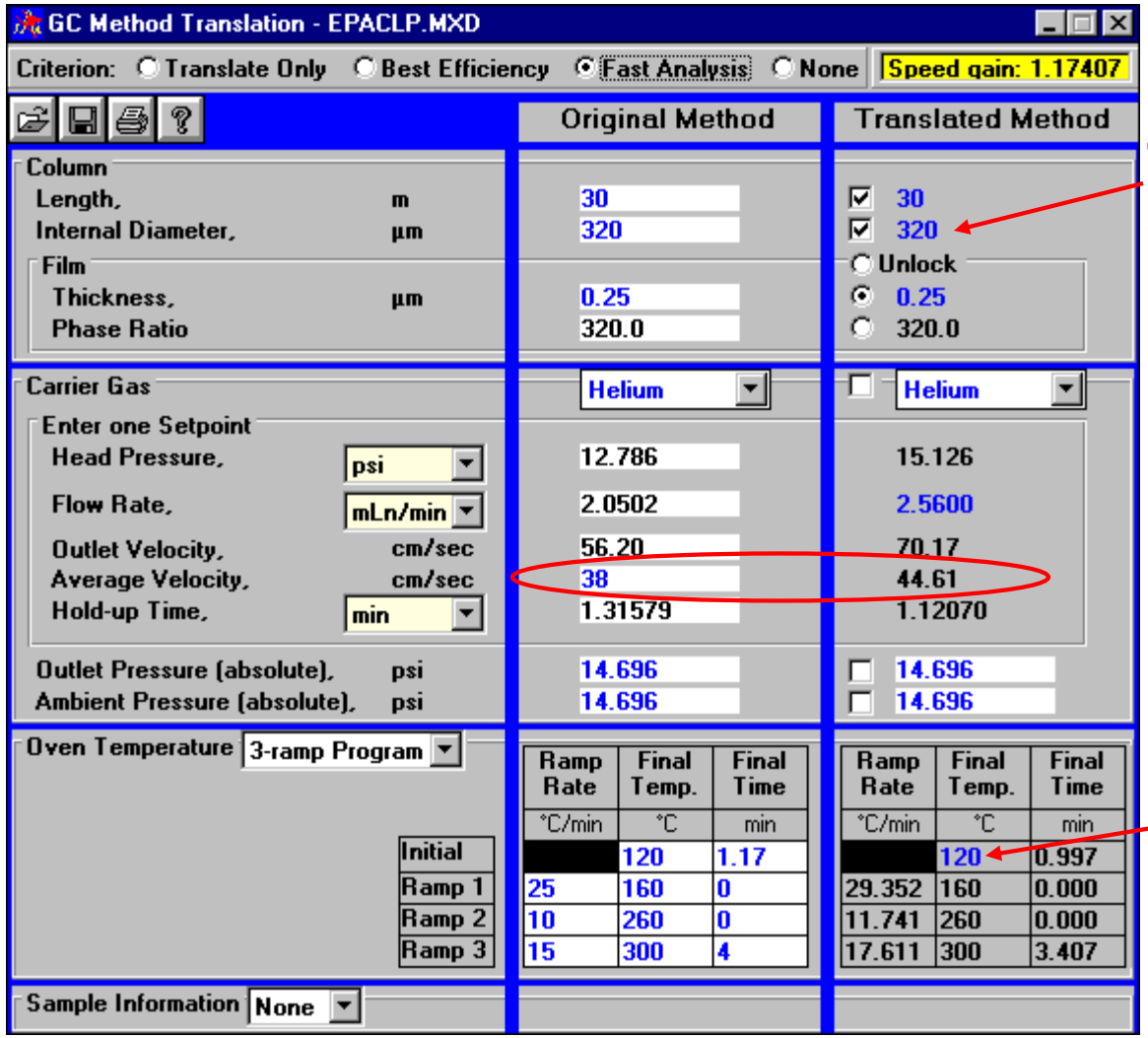
Input Original Method Parameters



Same Column and Gas Type
Fast Analysis (OPGV)



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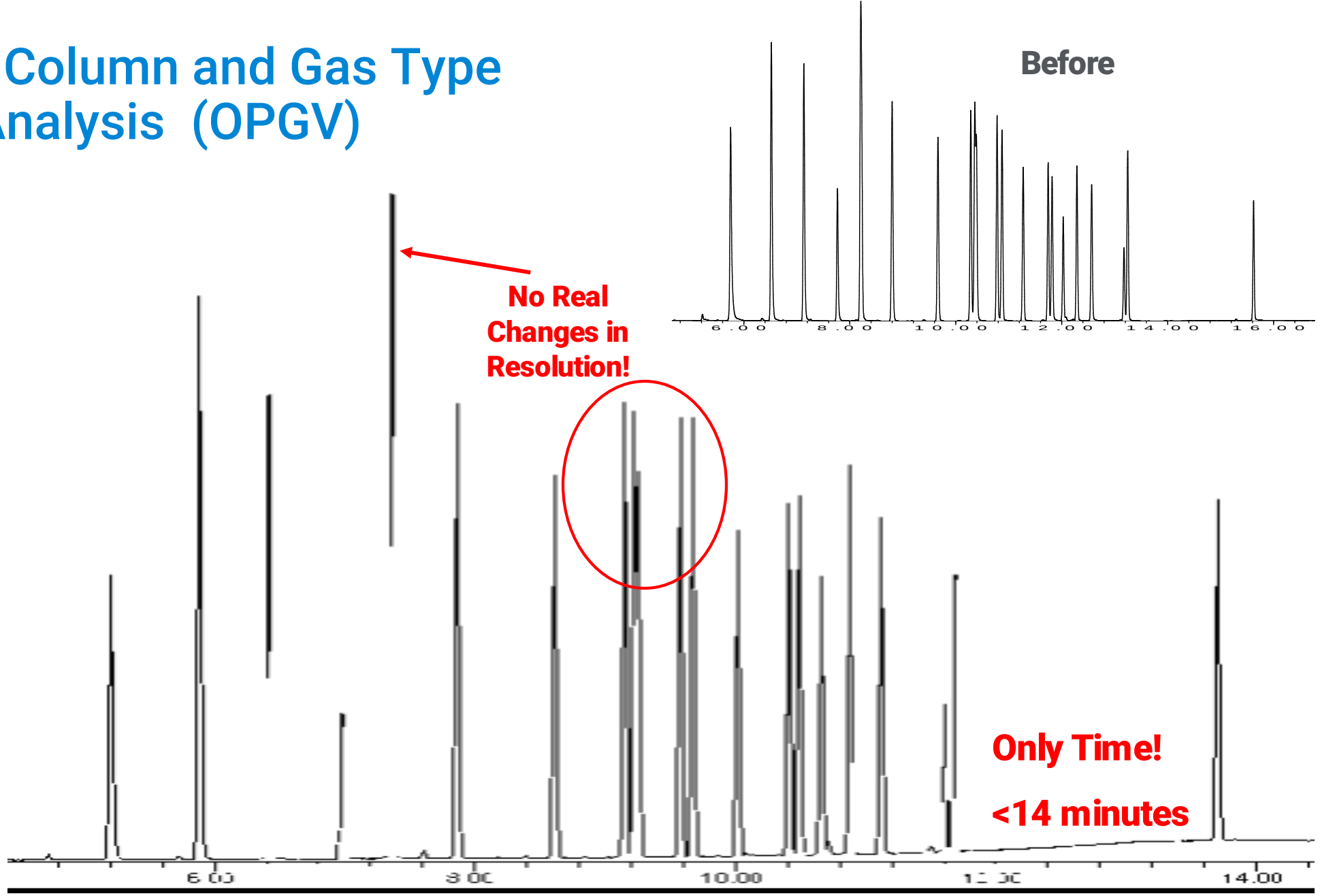
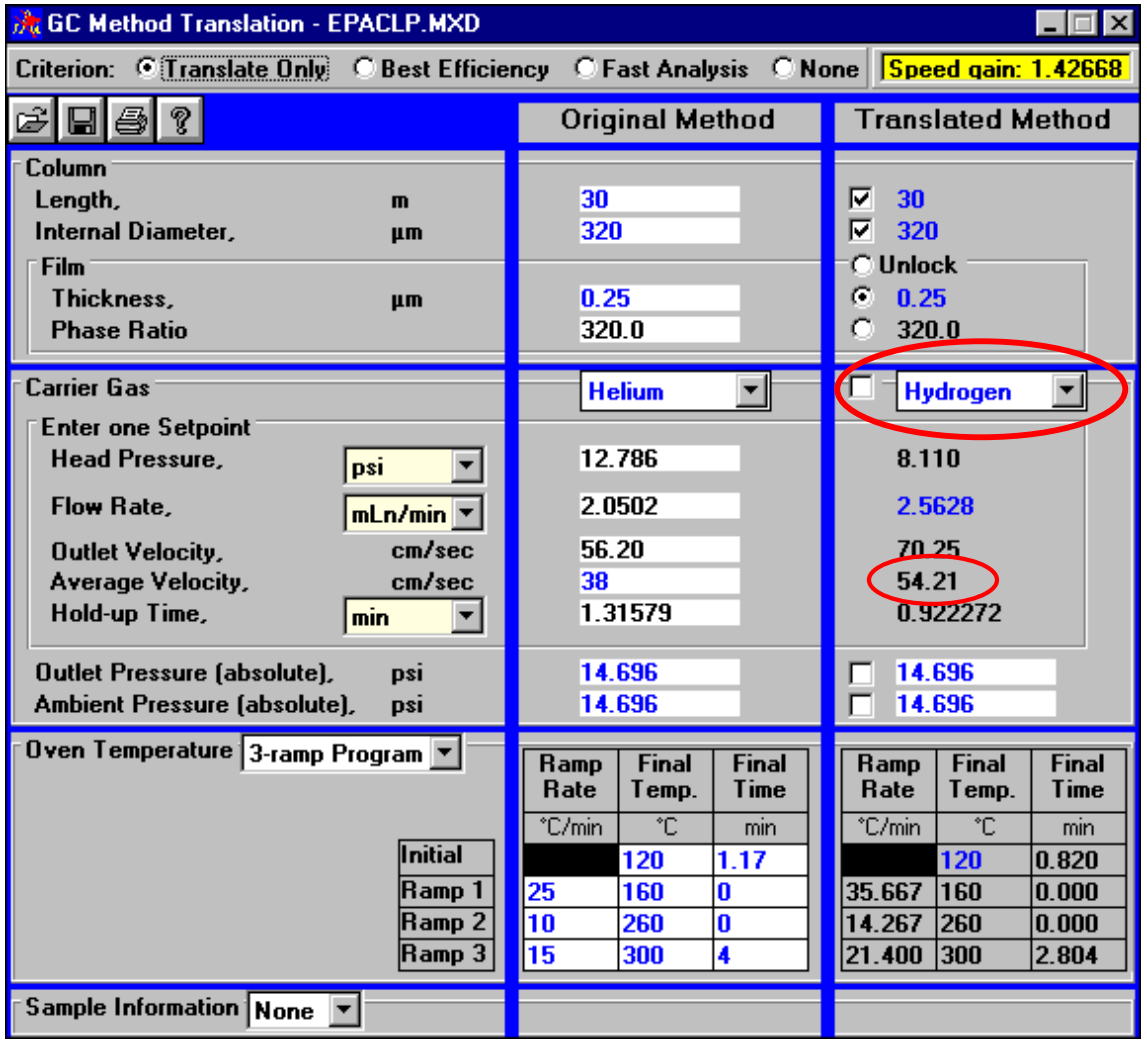
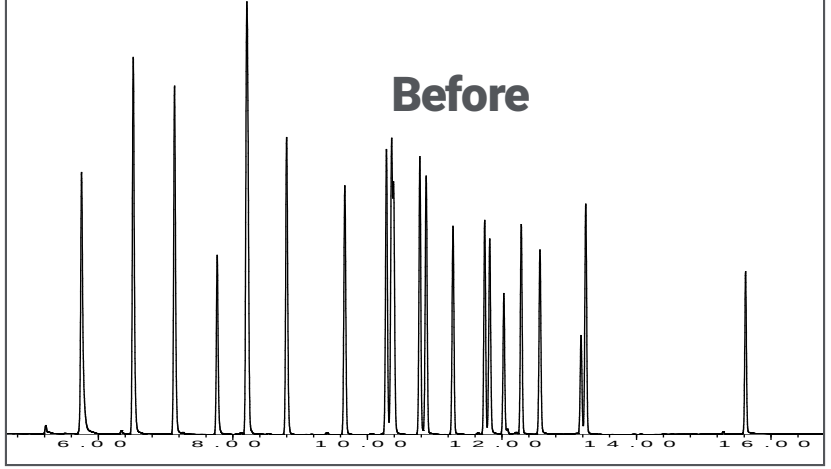
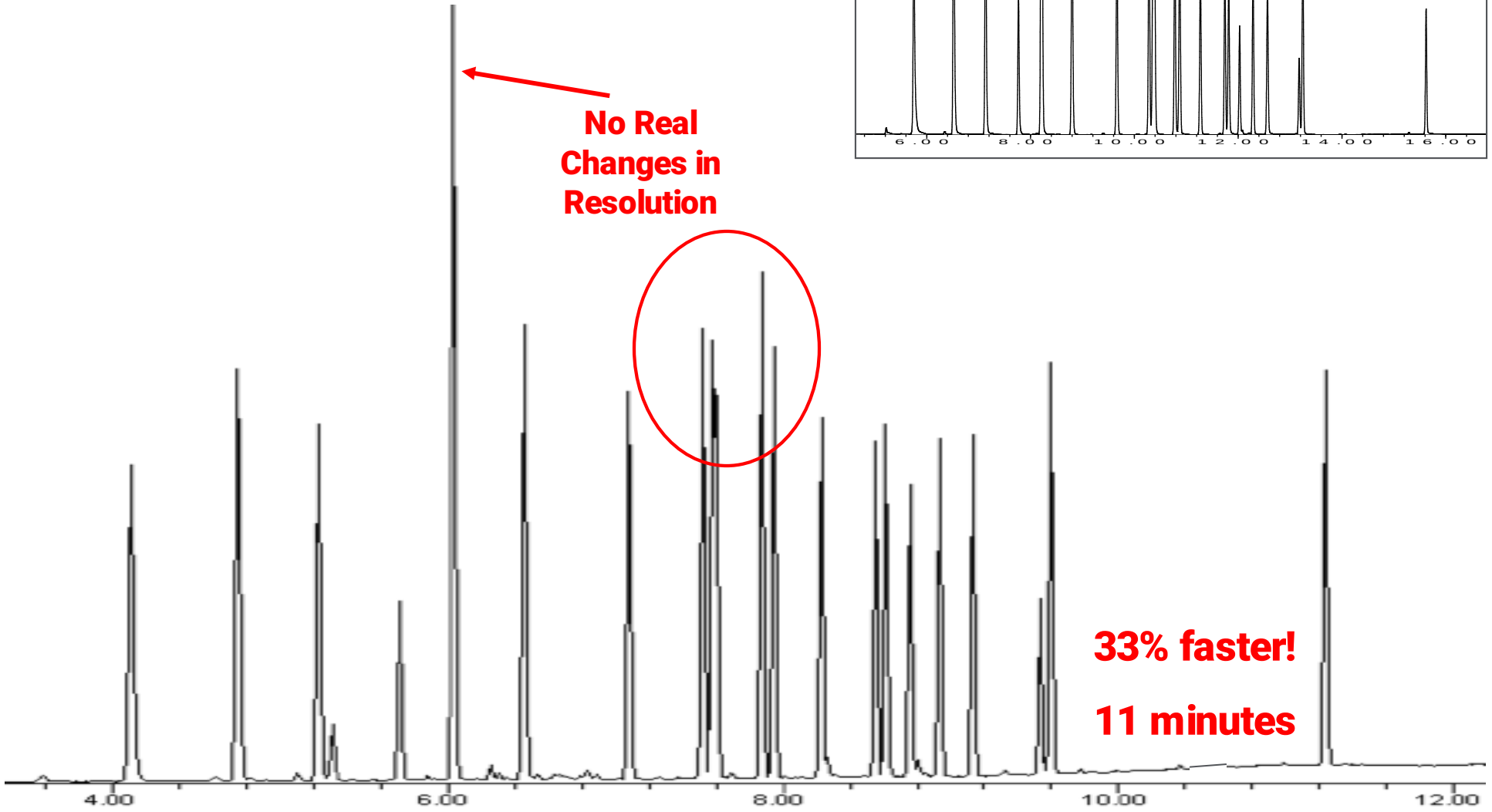


Same Column, Hydrogen Carrier Gas Translate Only



Same Column, H_2 Carrier Gas Translate Only





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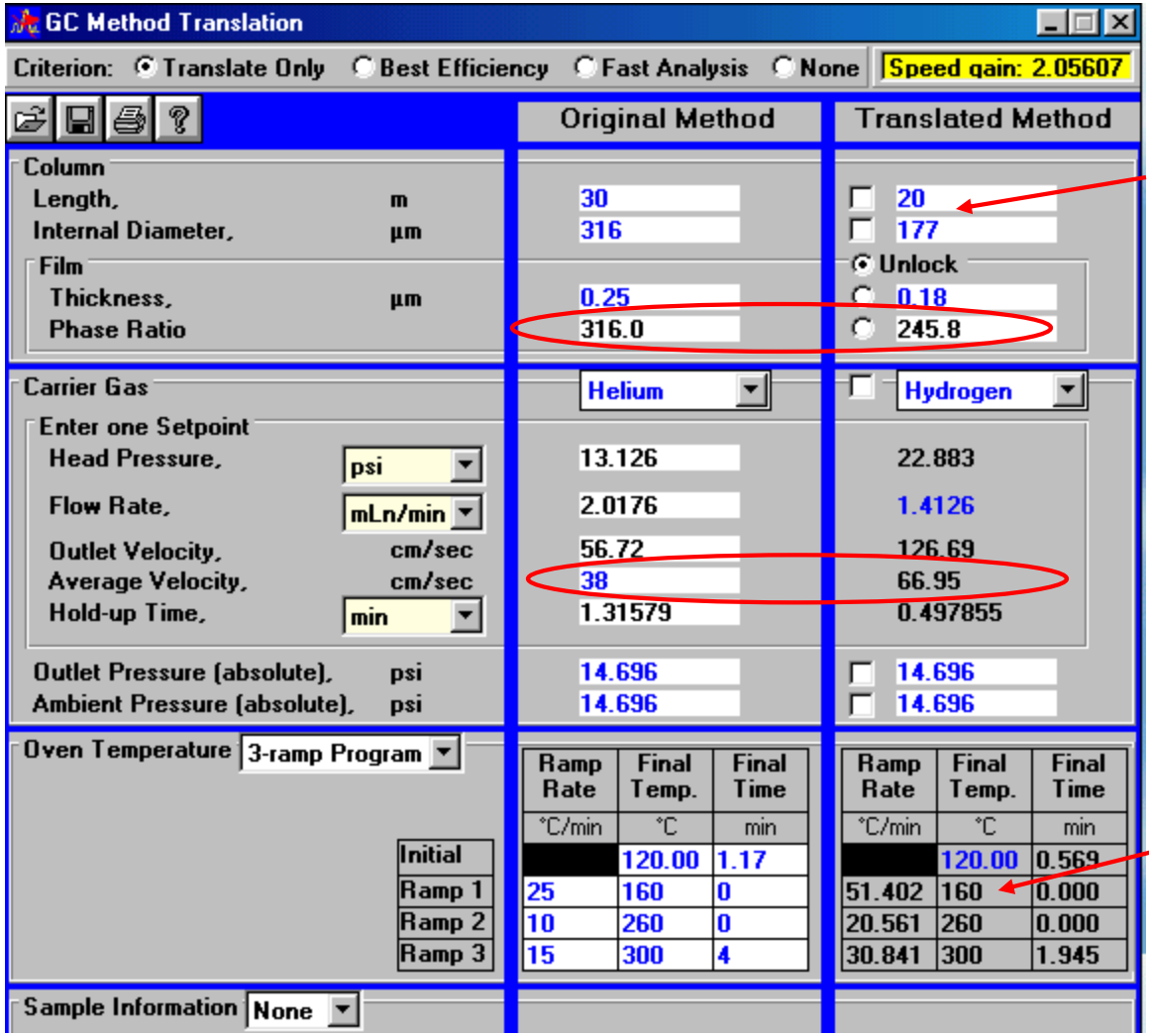
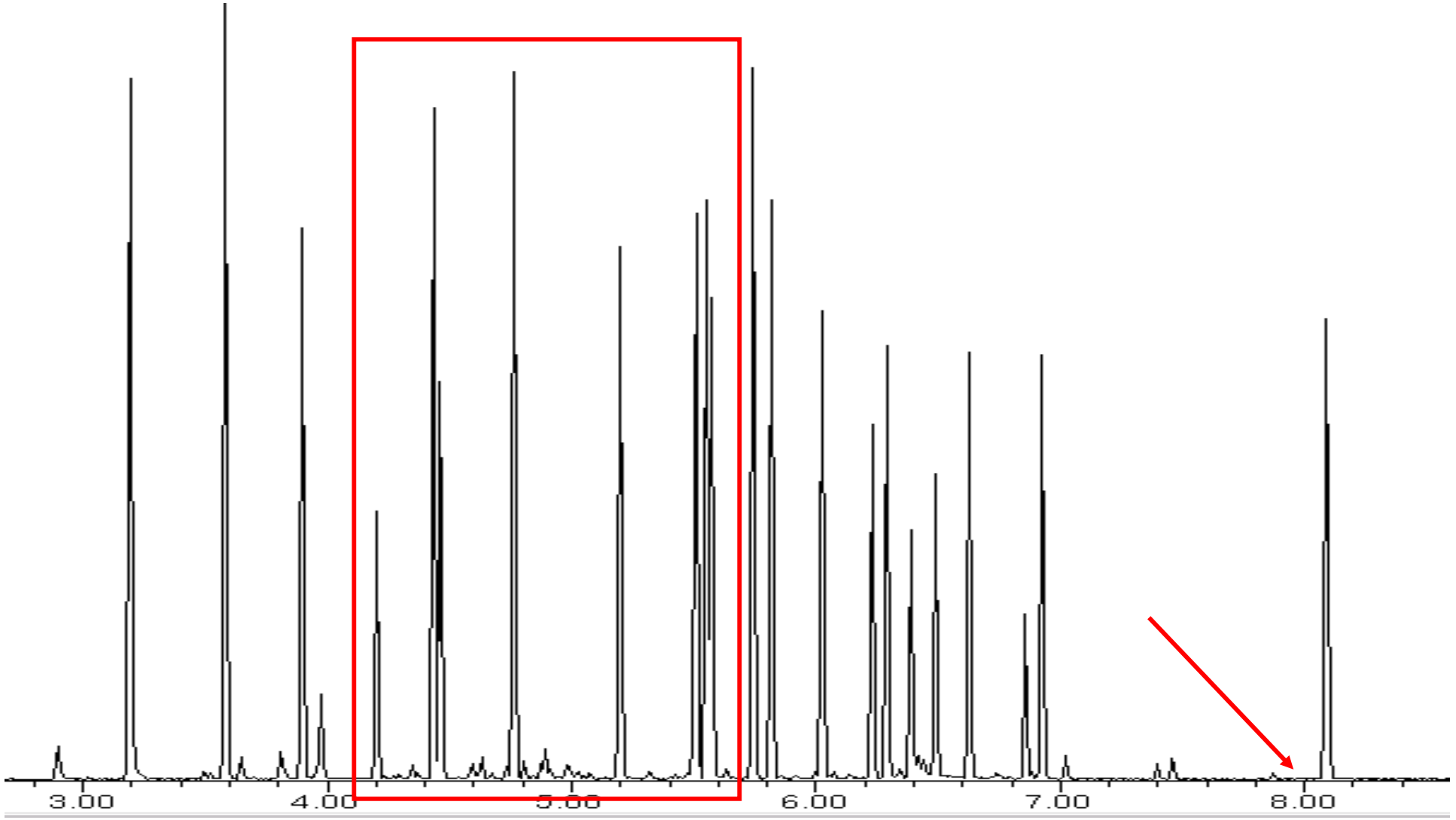
New Column Dimensions, H_2 Gas, Translate Only



New Column Dimensions, H2 Gas, Translate Only



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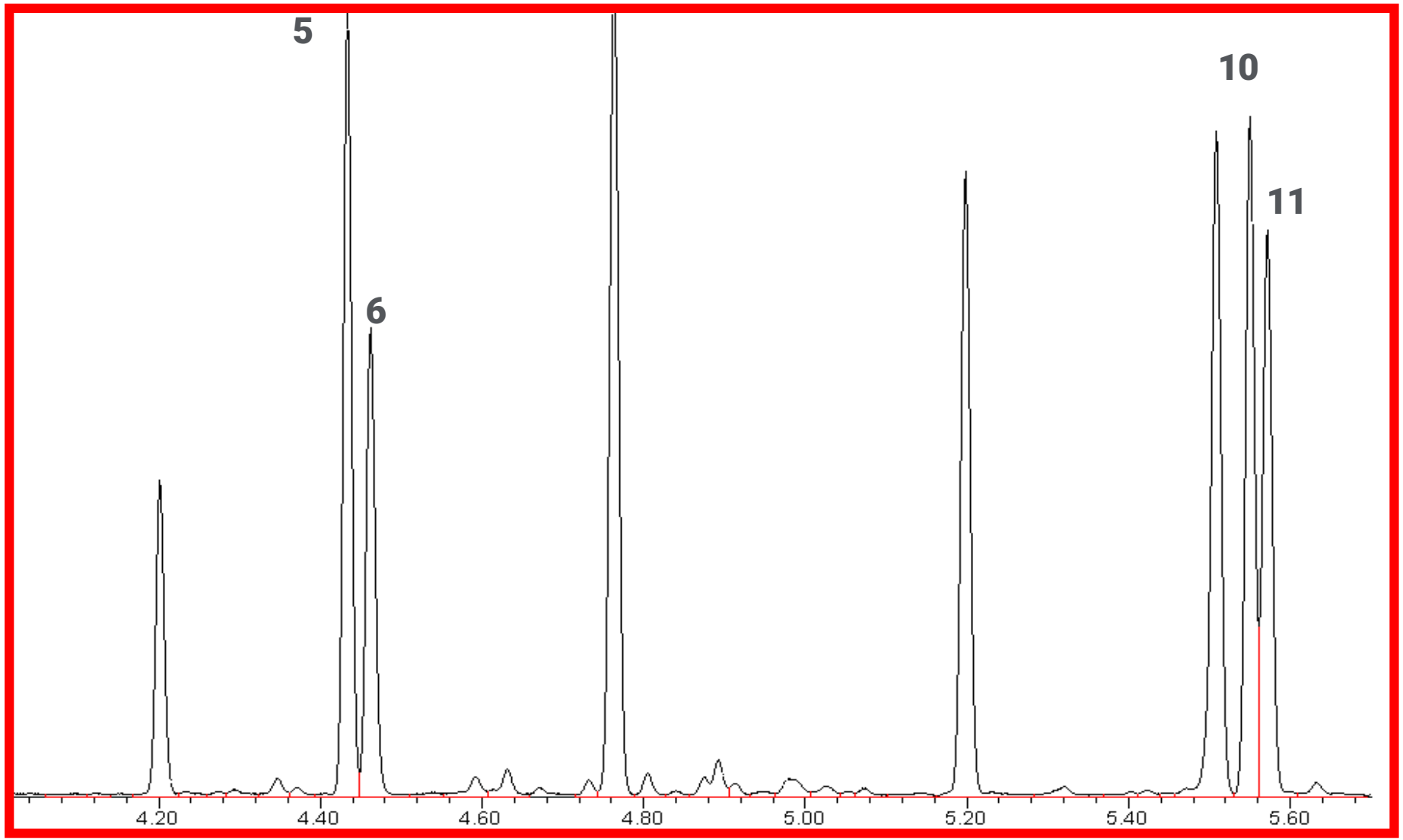

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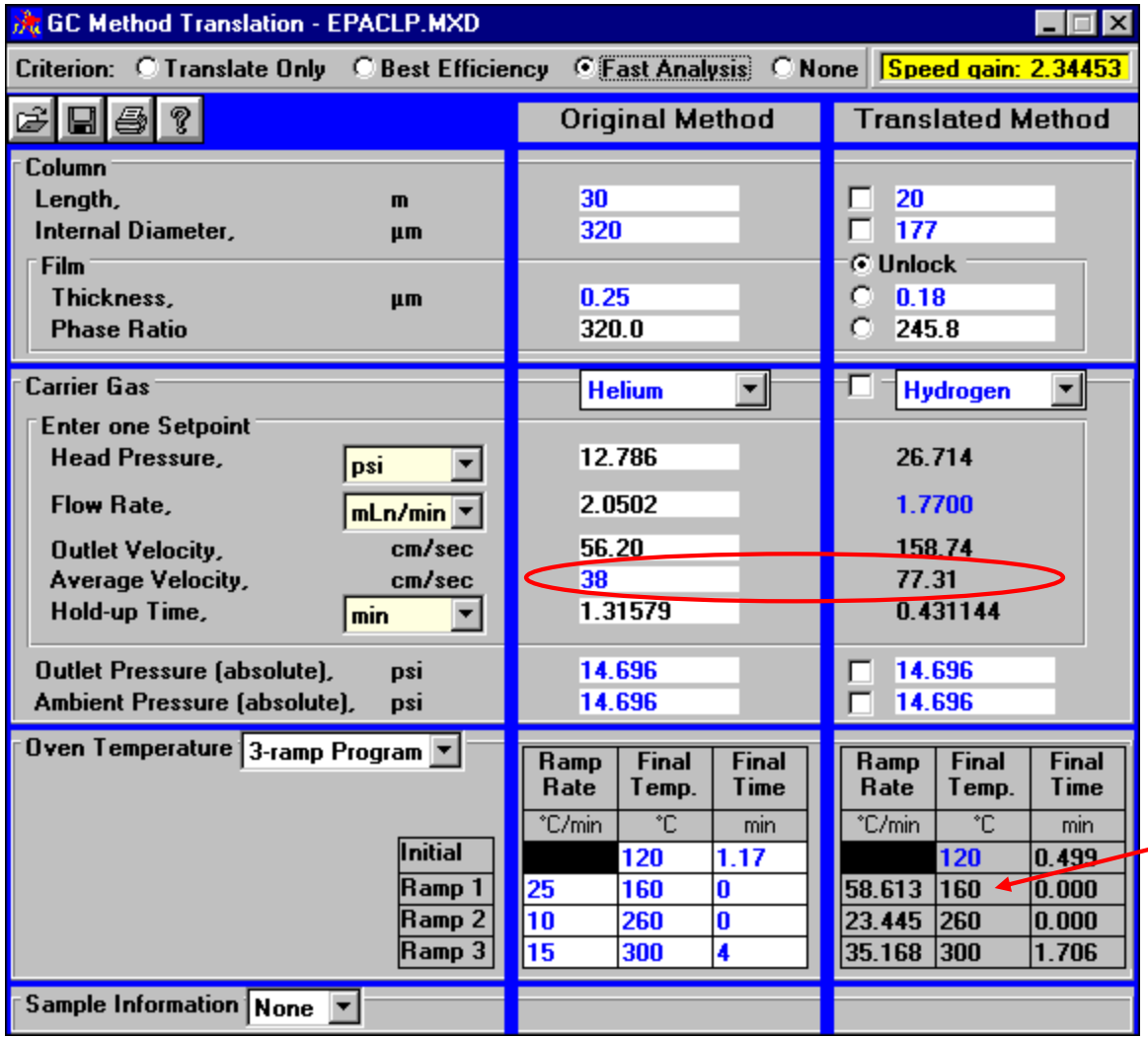
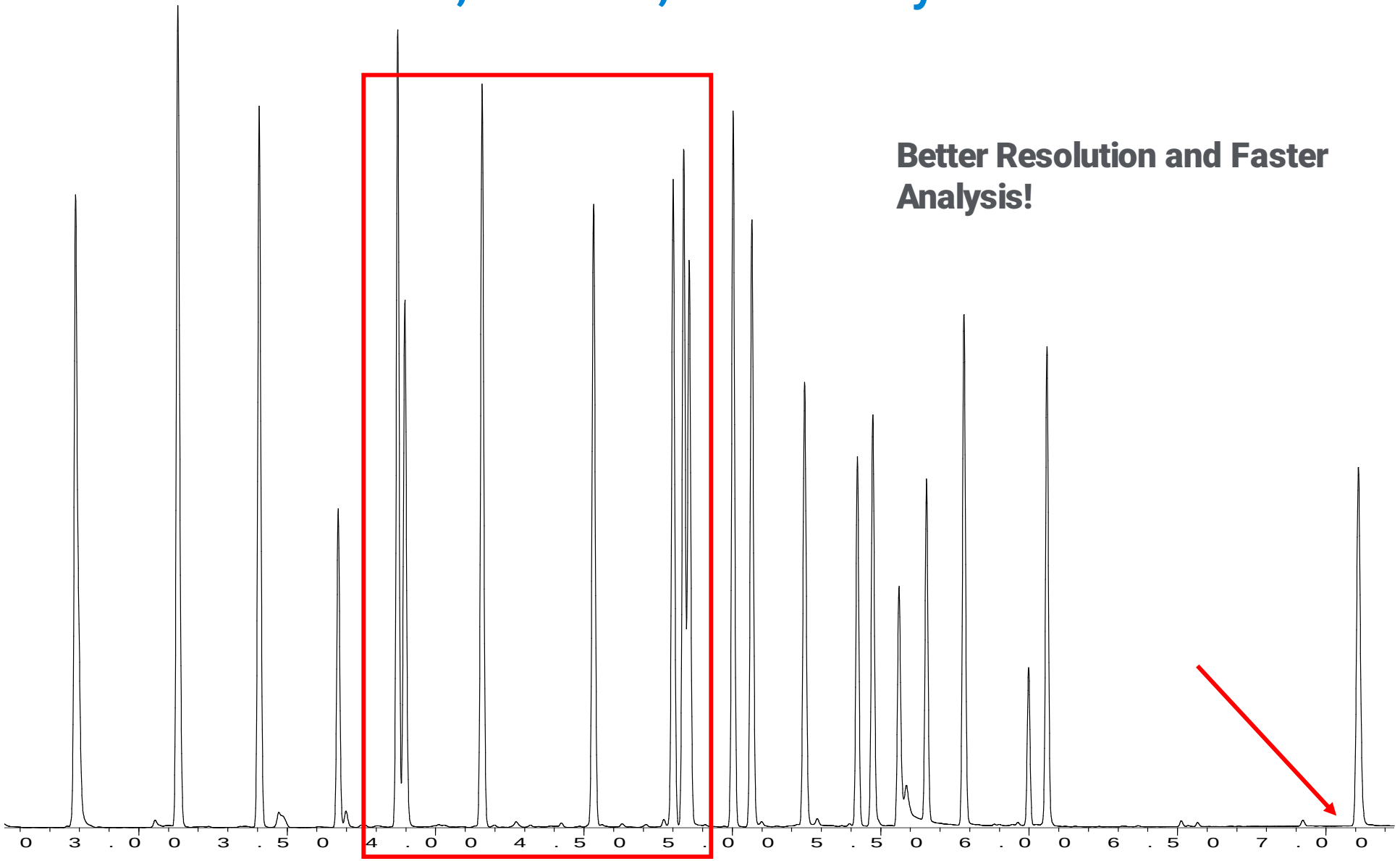
New Column Dimensions, H2 Gas, Fast Analysis



New Column Dimensions, H2 Gas, Fast Analysis



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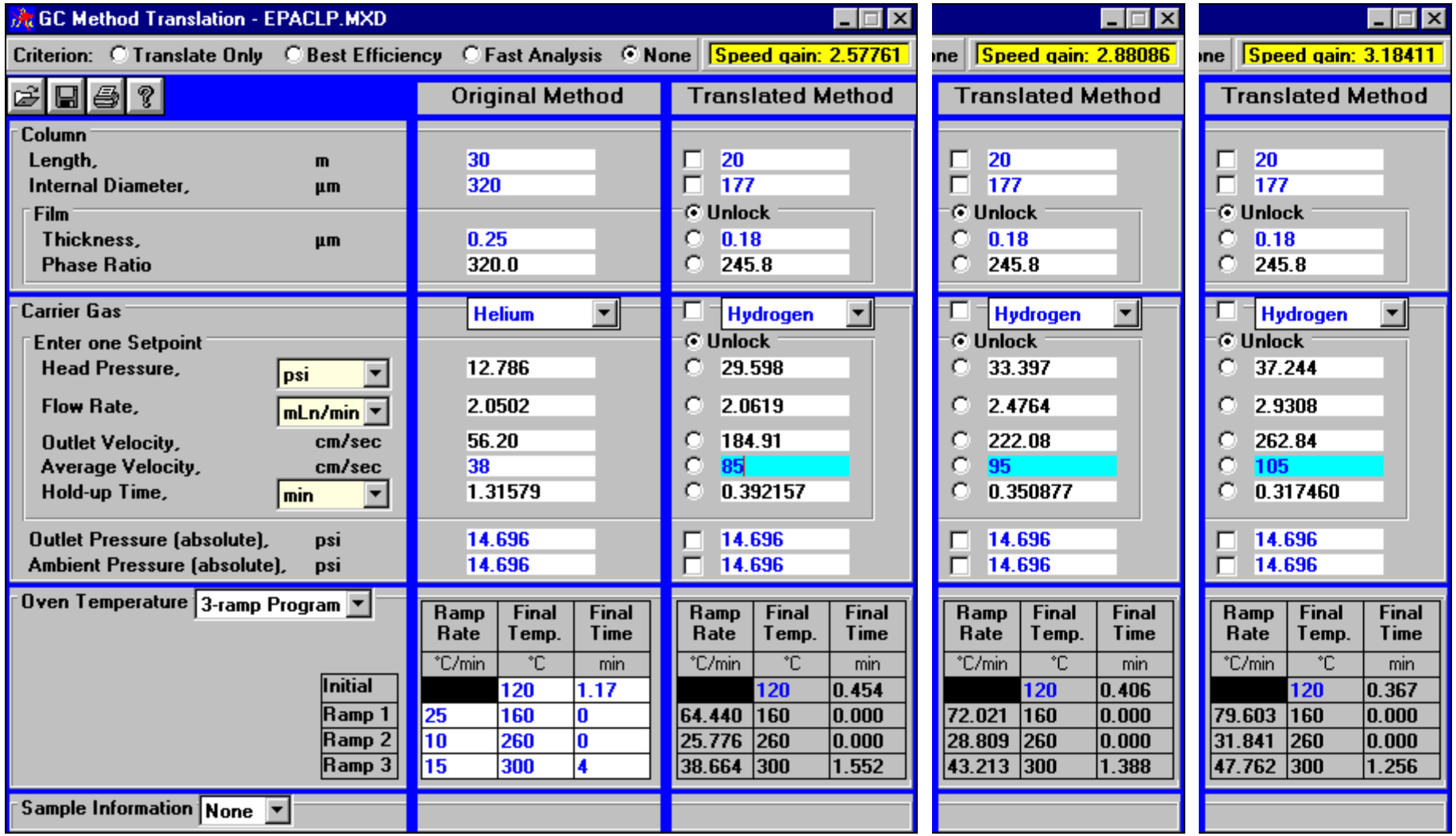
New Column Dimensions, H2 Gas, Higher Velocities



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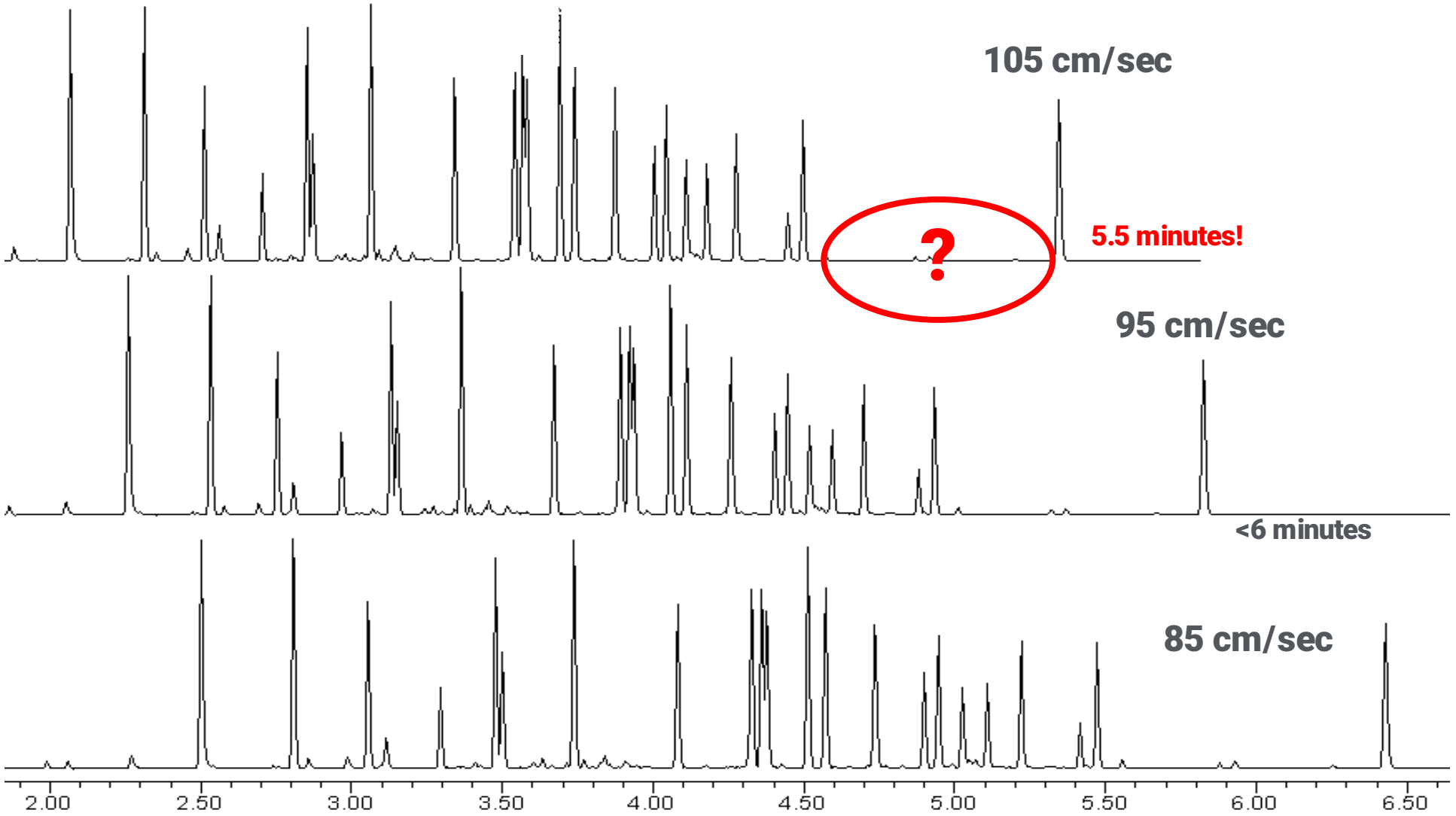
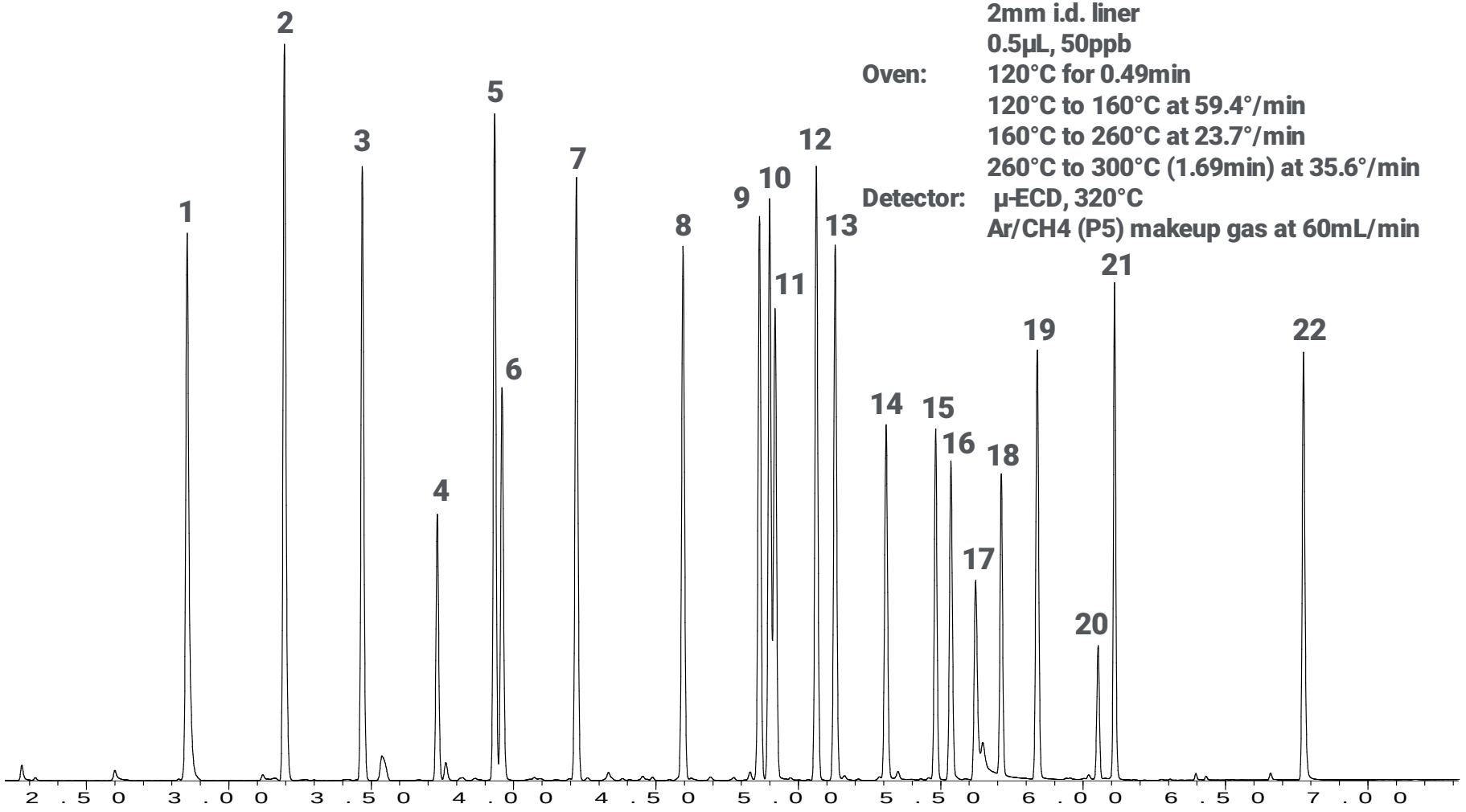


Final Method Used at EPA

Column: DB-XLB
20m x 0.18mm i.d., 0.18µm
Carrier: H2, constant flow, 77.3cm/s at 120°C
Injector: Pulsed Splittless, 220 °C
Pulse pressure & time: 35psi for 0.5min
Flow ramp at 6.25min of 99mL/min^2 to 3mL/min
2mm i.d. liner
0.5µL, 50ppb
Oven: 120°C for 0.49min
120°C to 160°C at 59.4°/min
160°C to 260°C at 23.7°/min
260°C to 300°C (1.69min) at 35.6°/min
Detector: µ-ECD, 320°C
Ar/CH4 (P5) makeup gas at 60mL/min



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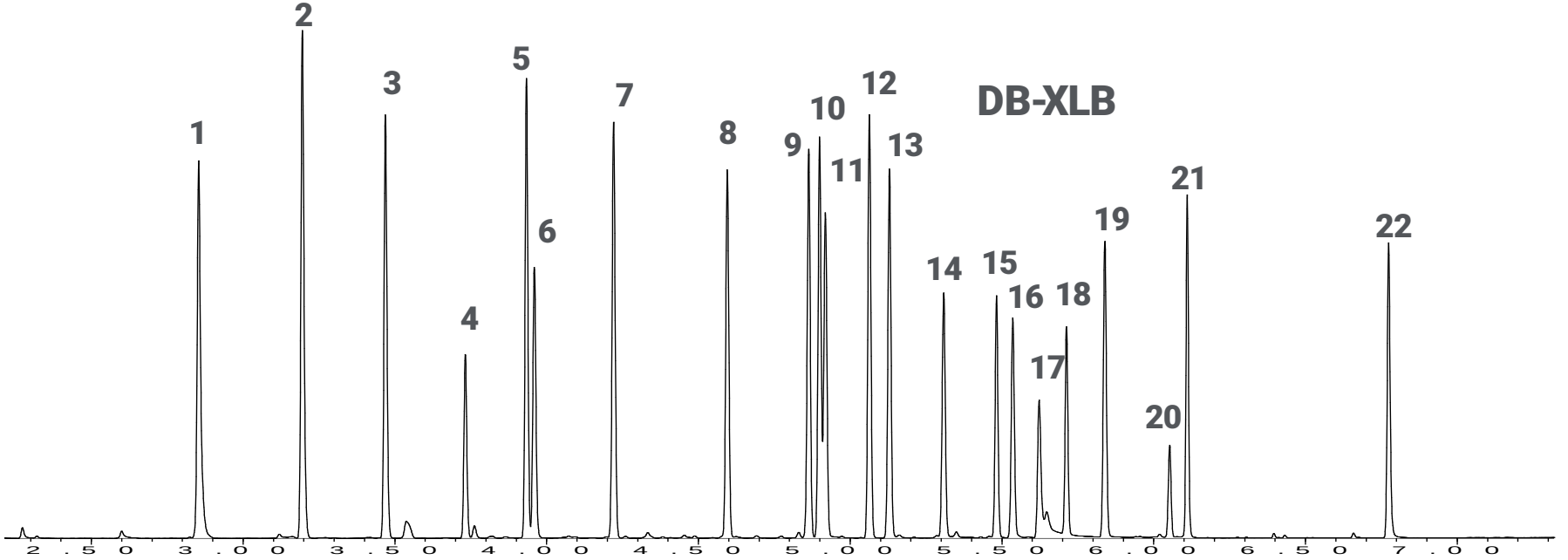

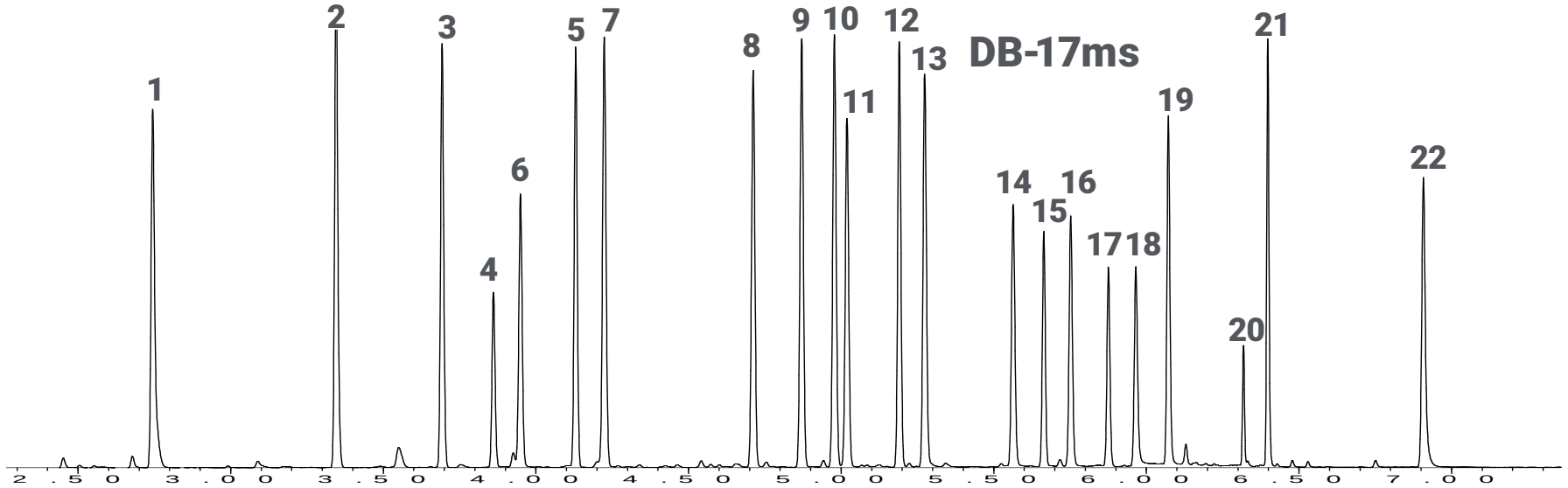

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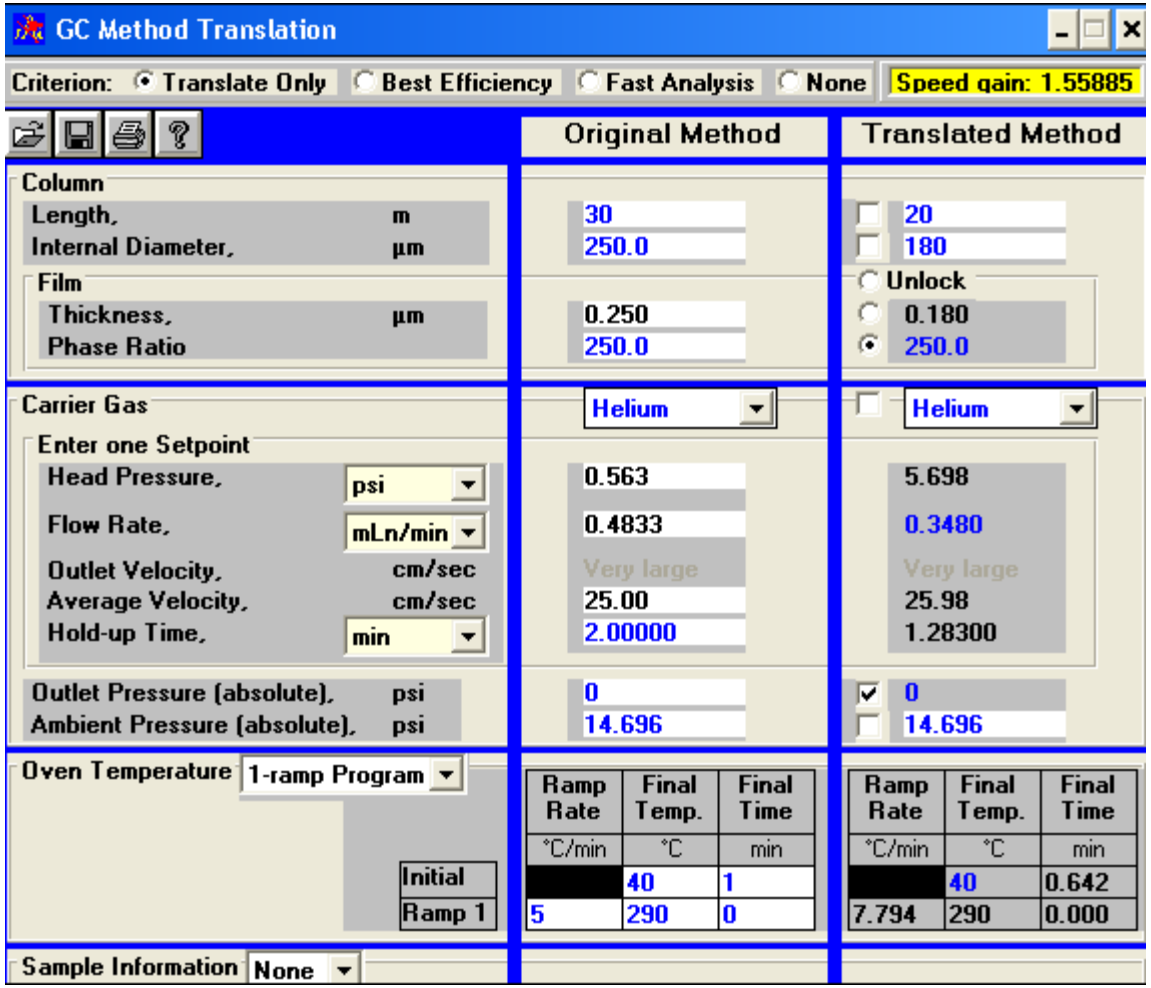
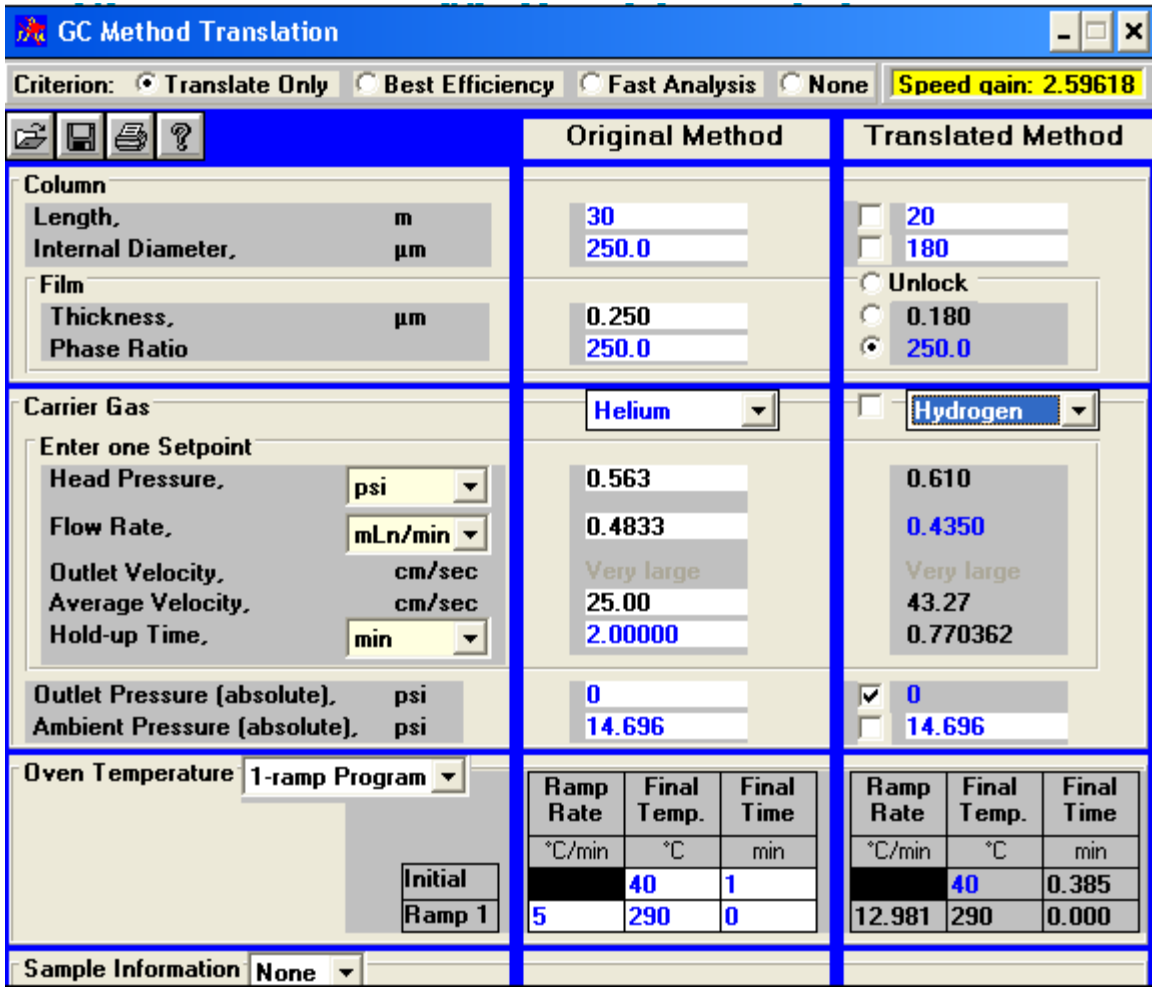
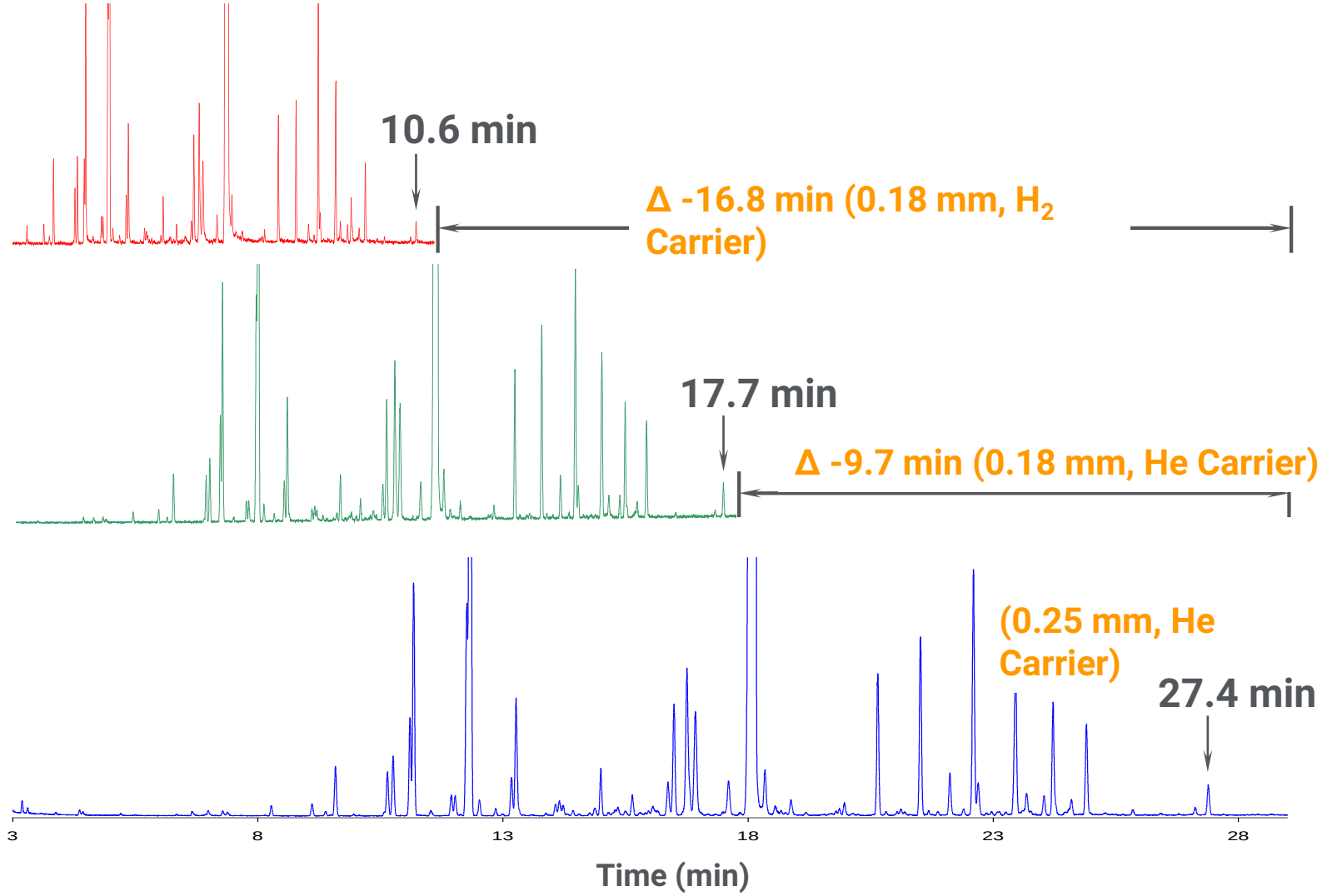
Food/Fragrance – Method translation



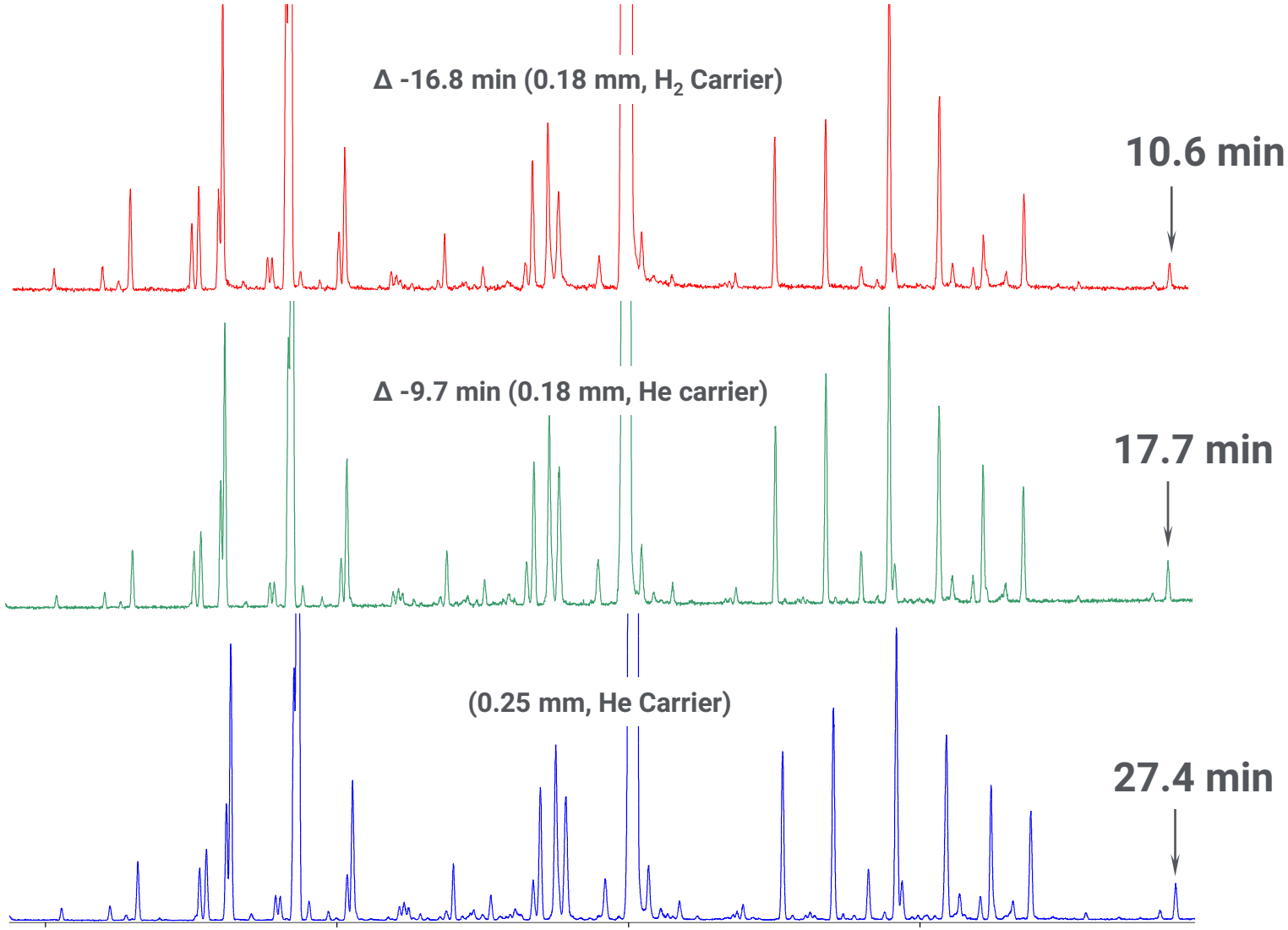
Food/Fragrance – Method translation



Spearmint Oil



Spearmint Oil – Resolution Check



Resolution Maintained

Compound Resolution			
Compounds	**0.25 mm Helium**	**0.18 mm Helium**	**0.18 mm Hydrogen**
Sabinene β-Pinene	1.52	1.59	1.56
α-Terpinene p-Cymene	1.61	1.73	1.86
Speed Gain	**N/A**	35%	61%

CONCLUSIONS

Stationary Phases – Chosen for optimized selectivity

Diameter – Smaller allows shorter length but has less capacity

Make Small Changes – Again think capacity

Carrier Gas – Hydrogen, high velocity, but can still go fast with He

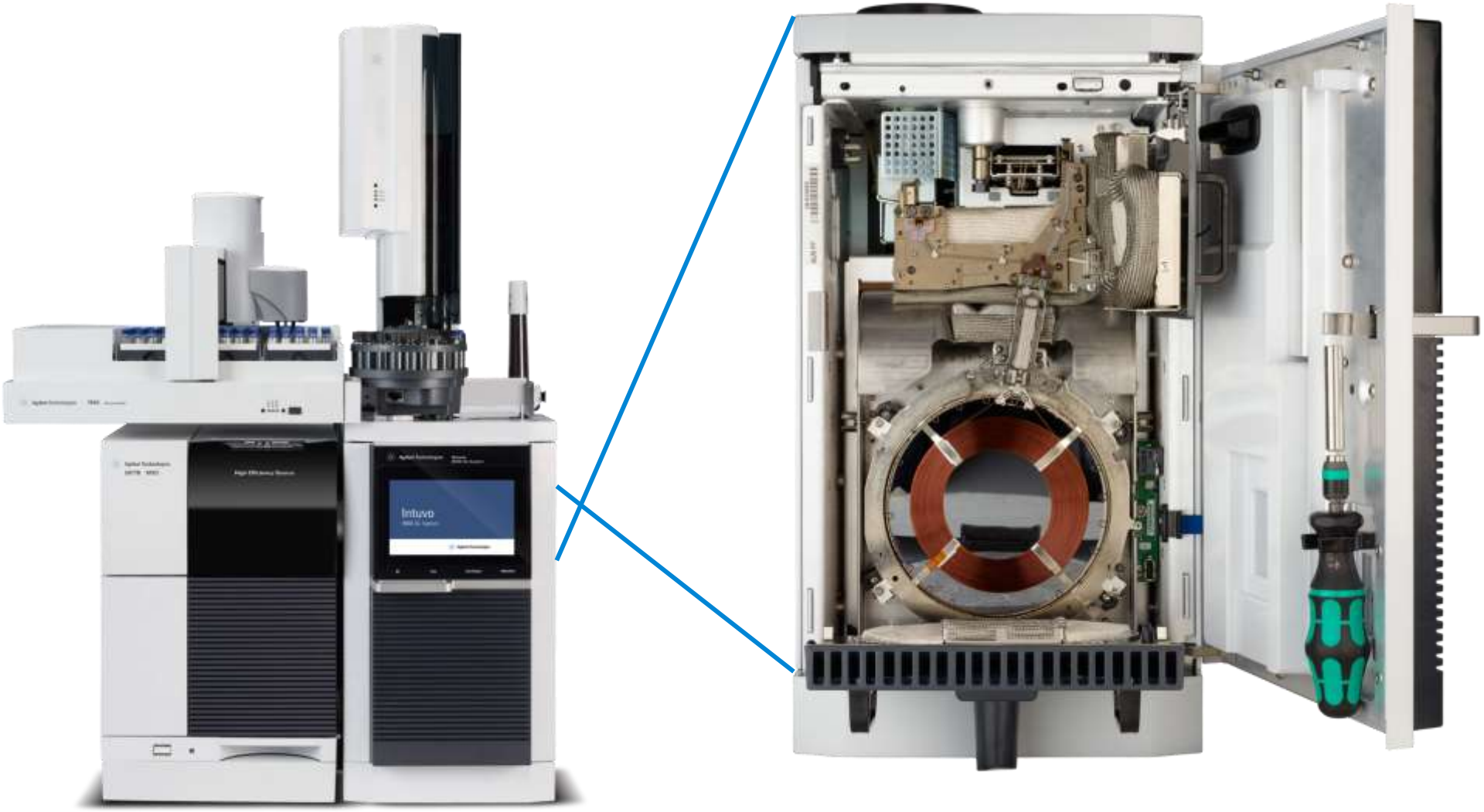
Temperature Program – Scale properly to preserve elution pattern

Method Translation Software – FREE, reliable

Flow Ramp – Increase at end of run for late eluters (if necessary)

System Upgrades – LTM, Capillary Flow Devices (back flush)

The New Agilent Intuvo 9000 GC System



Common frustrations with GC

- **Measuring column length correctly**
- **Cutting your column correctly**
- **How tight it too tight?**
- **Clipping columns to deal with active sites, then updating retention times**

Common Care and Maintenance Scheme for GC Columns

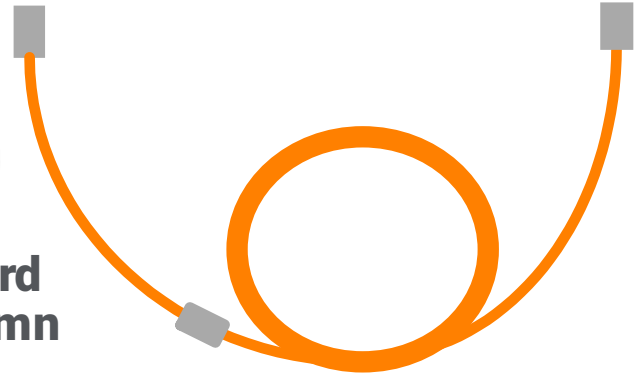
1. Cut off 6”-1ft of the inlet end of the column.

2. Bake out the column for no more than 2 hours.

3. Cut off more column. (repeat as necessary)

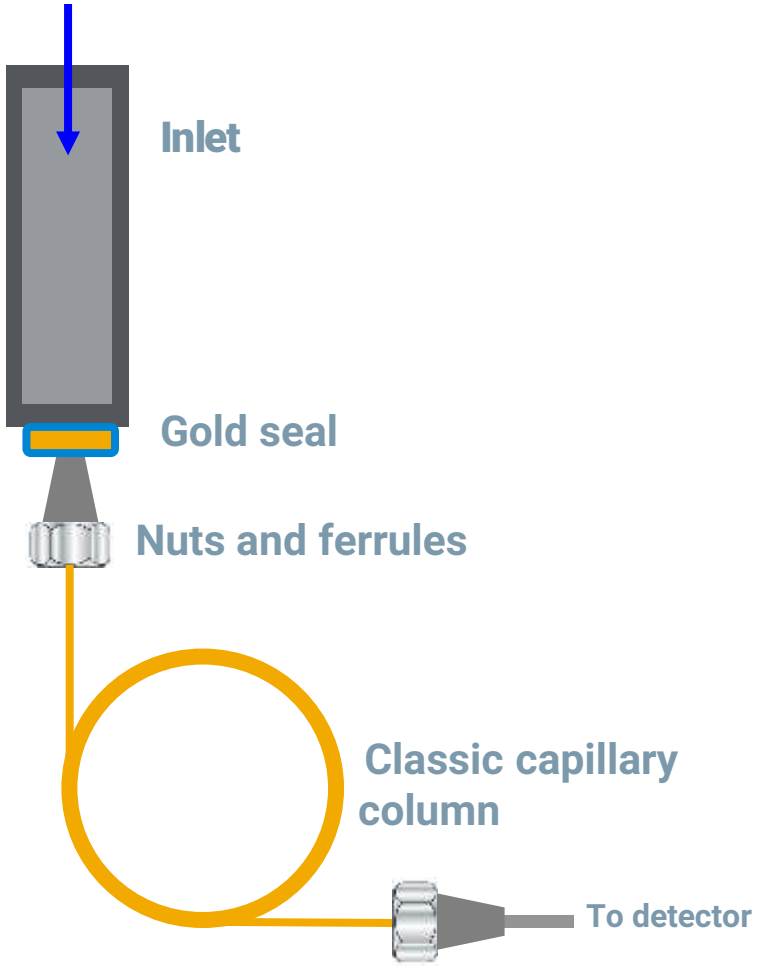
Intuvo…

Change the guard chip

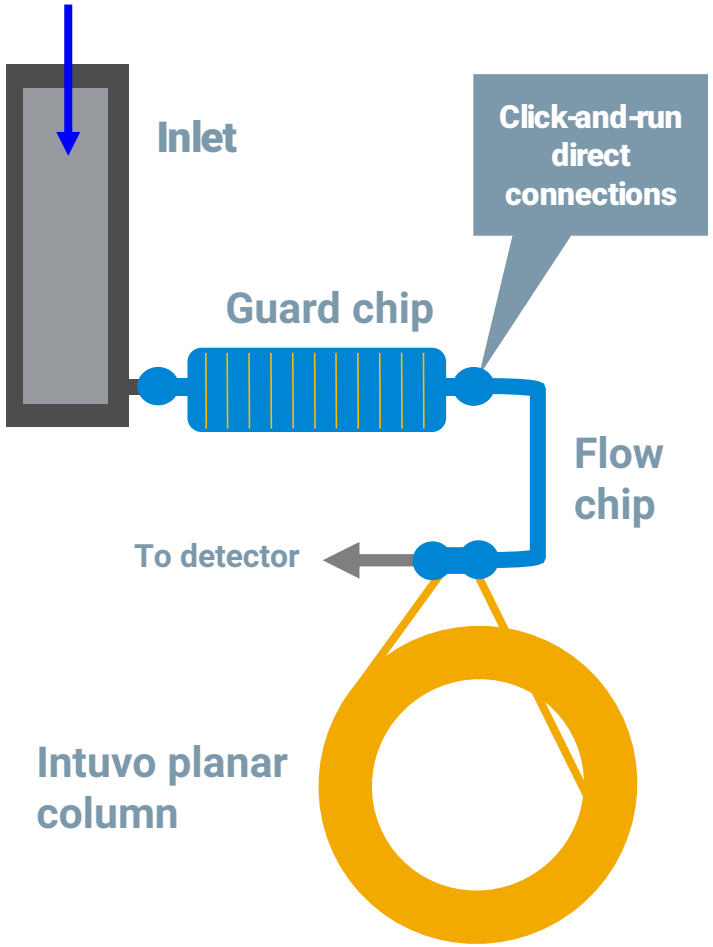


Innovating the GC Flow Path

Conventional flow path

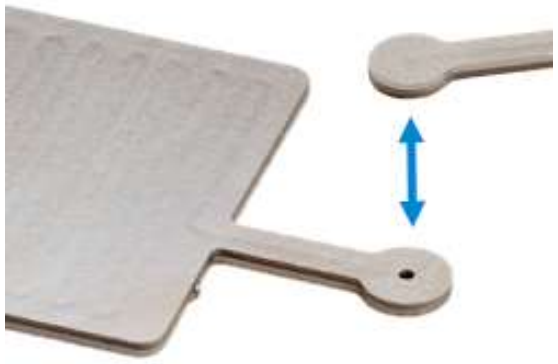


Intuvo flow path



Easier and faster maintenance with Intuvo

- No more ferrules
- Direct face seal connections
- Audible and tactile click lets you know connection is made
- Less unplanned downtime
- Fewer batch reruns and precious samples lost

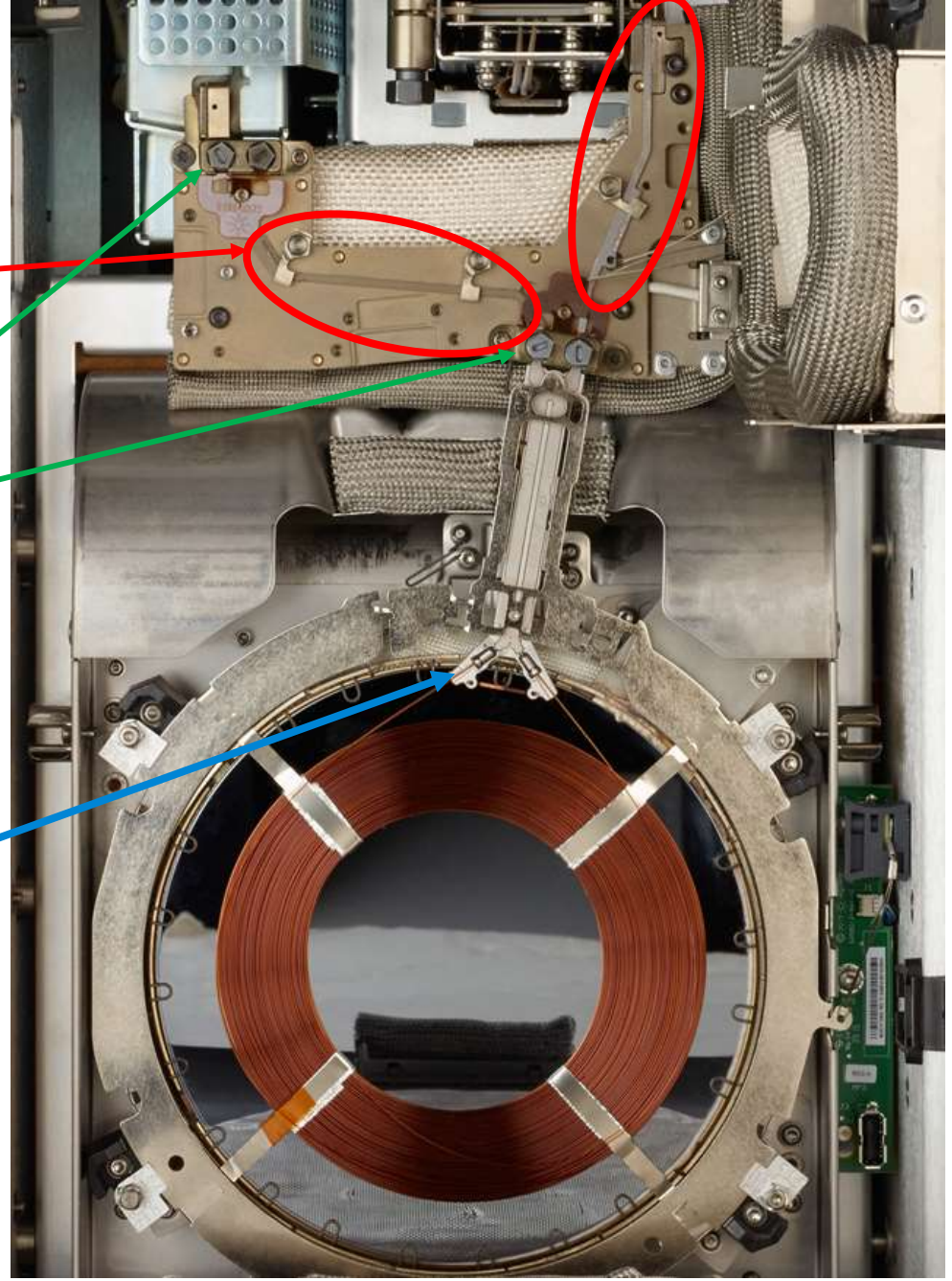


No More

- measuring

- over-tightening

- trimming



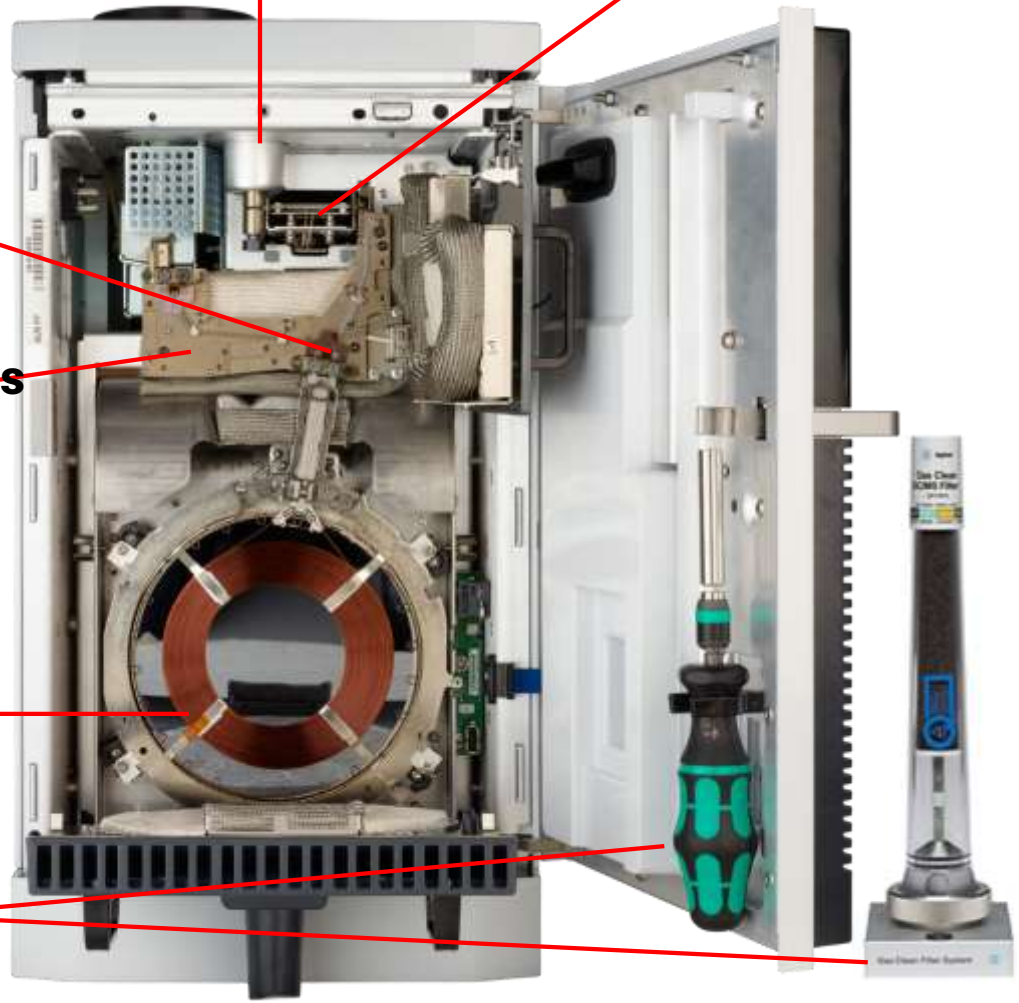
A New Portfolio of GC Consumables

UI Inlet Liners

Guard Chip

Smart Keys

Intuvo Flow Chips



No-trim column

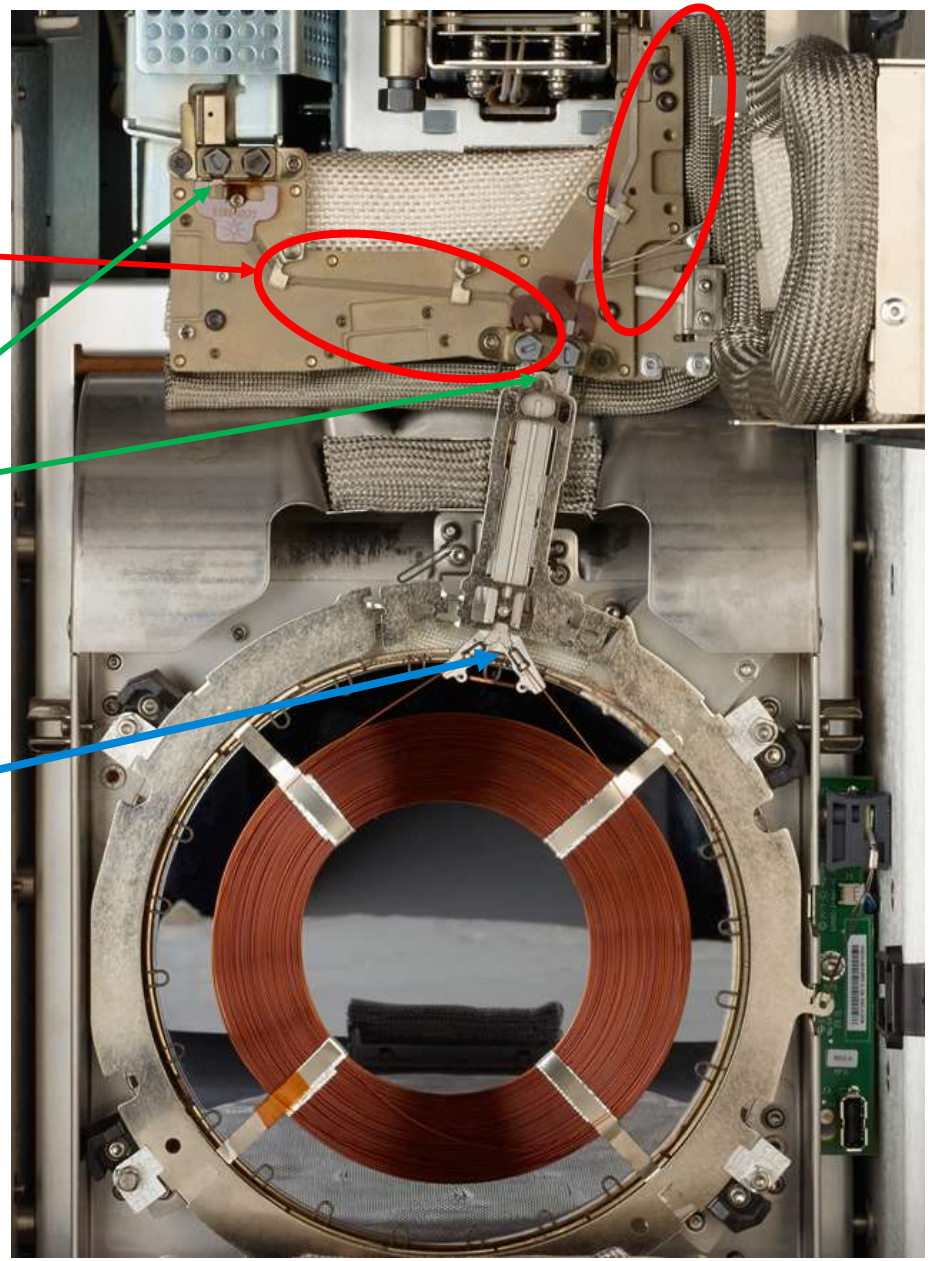
Tools & Accessories

No More:

- Measuring

- Over-tightening

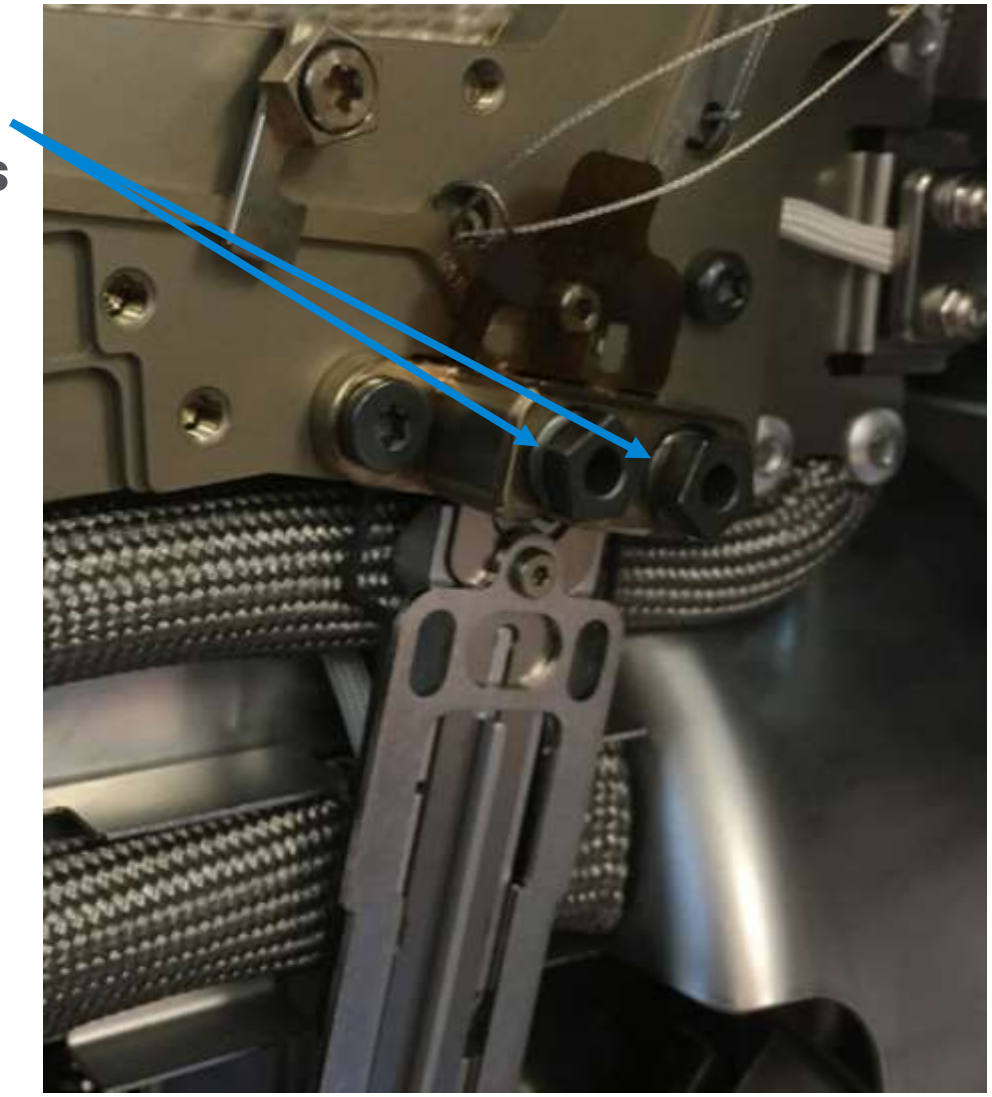
- Trimming



Tips to Assure a Good Column Installation

1. **Finger tighten until only 1 thread on each of the two nuts is showing.**

If more than 1 thread is showing, wiggle or re-position the column into place to further finger tighten the nuts to 1 thread.

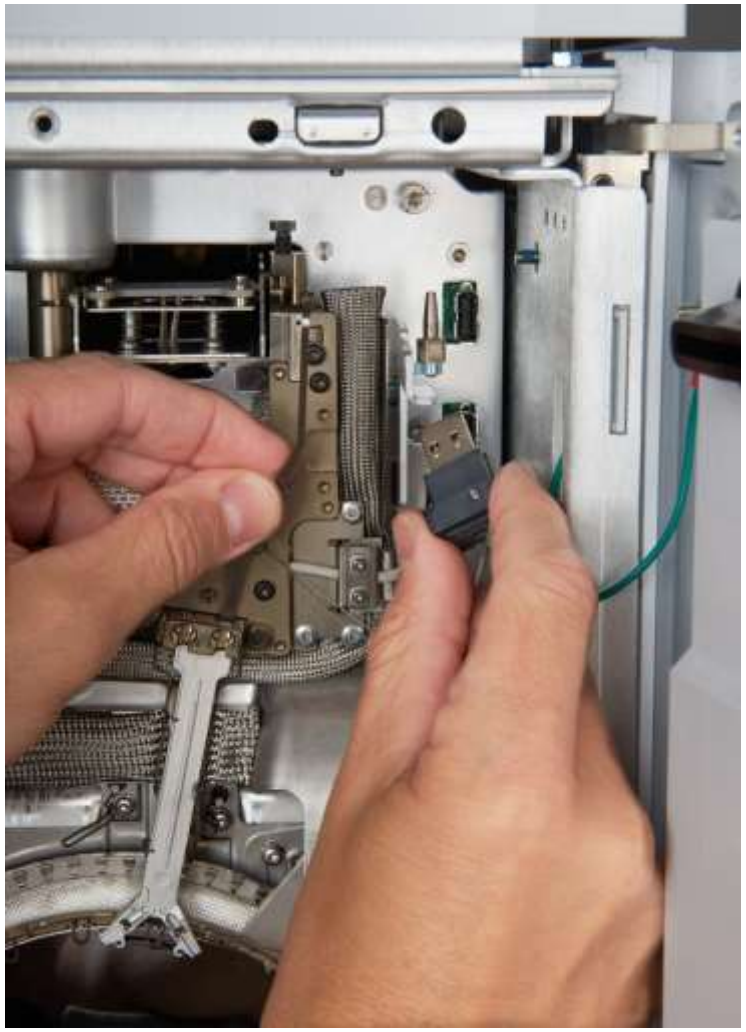


Tips to Assure a Good Column Installation

2. **Check that the small integrated column nuts on the column are in form fitted place on the heater in the instrument.**
3. **Click and Run!!**

Smart Key Technology

- Smart chip tells your Intuvo what you have
- Sets temperature limits for you
- Keep track of performance with read/writeable Smart Key



Where Does it Get Dirty?

Here

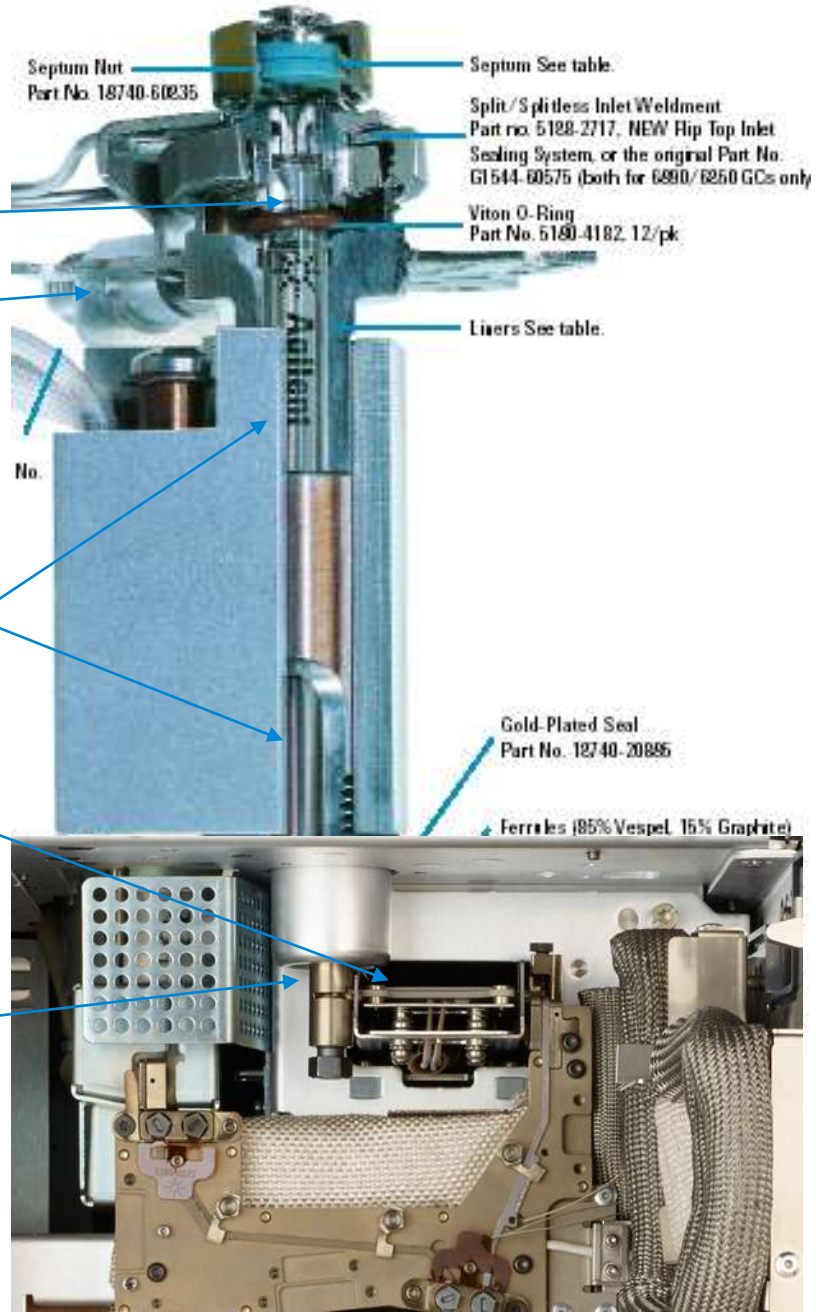
Here

Here

Here

Here

Here



Not the Column!

New Autonomous Leak Checking